BIOLOGICAL DESTRUCTION OF CYANIDE IN CANADIAN MINERAL PROCESSING EFFLUENTS

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October 4, 1985

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Dear Dr. Shan:

RE: DSS FILE NO. 15SQ.2344-4-9184
CONTRACT SERIAL NO. OSQ84-00287
TITLE: BIOLOGICAL DESTRUCTION OF CYANIDE
IN CANADIAN MINERAL PROCESSING EFFLUENTS

In completion of all requirements of the above contract, we submit ten copies of the final report. An executive summary in both official languages is also included.

We are confident that you will be pleased with our evaluation. Please feel free to contact us in the future whenever we can be of assistance.

Yours Sincerely,

F. Tonelli
Vice President - Technical Services

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EXECUTIVE SUMMARY

A literature review was undertaken to determine whether biological treatment processes can benefit the Canadian mineral processing industry for the treatment of cyanide bearing wastewaters. The evaluation process consisted of two stages. First, information pertaining to biological processes, used for the treatment of cyanide bearing wastewaters, was gathered and summarized in the form of an interim report. The second stage of the evaluation consisted of a critical review of processes identified in stage one, in order to select a candidate process(es) for biodegradation studies. Information gaps which require further research, prior to practical application of the proposed process were also identified. The results of both stages of evaluation were summarized in the final report.

The biodegradability of cyanide is influenced by many factors. These include:

i) The chemical characteristics of the wastewater streams to be treated (cyanide levels, form of cyanide, heavy metal concentrations, variability, concentrations of other chemical species).

ii) The characteristics of the microorganisms (rate of growth, nutrient requirements, cyanide concentrations tolerable, rate of cyanide uptake, type of cyanide degradable, optimum pH and temperature ranges for growth, inhibitors).

iii) The process characteristics (loading rates permitted, sensitivity to shock loads, fate of cyanide in the system, sludge settleability, availability of nutrients and oxygen, biomass control).

During the literature review, particular attention was given to these details. This information was used in the screening of the biological processes and wastewater types.

Cyanide bearing effluents, produced by five mineral processing industries, were considered:

- Gold milling barren bleeds, tailings repulp and tailings impoundment streams
- Silver milling wastewaters
- Base metal sulfide flotation tailings liquors
- Coke oven and blast furnace blowdown wastewater by-products during iron manufacturing
- Potlining leach liquors from the electrolytic cells used in the production of aluminum from bauxite.

The most important factor determining the biodegradability of cyanide in a given wastewater type, is the thermodynamic stability of the predominant form of complexed cyanides in solution. Very stable metal cyanide complexes, such as those of iron and cobalt are not readily biodegradable. However, they are less toxic than weakly bound complexes and have been reported to pass through biological treatment systems without inhibitory effects. Moderately stable complexed cyanides are partially biodegradable. Free cyanides are completely biodegradable. With this in mind, the treatability of the various cyanide bearing wastewater streams were evaluated.

The wastewaters recommended for further investigation are those from gold and silver mills. The biological treatment of iron and steel industry wastewaters is already well established and consequently does not require a detailed investigation. Tightly bound

iron cyanide complexes predominate in the tailings wastewaters of the base metal mines and the potlining leachates of the aluminum manufacturing industry. Consequently, these wastewaters were considered to be unsuitable candidates for biodegradation studies.

Bacteria which metabolize free and weakly complexed metal cyanides were identified (see Table 7.1.1). Microbial seeds can be obtained from locally collected microflora or, one of the many organisms reported to degrade cyanide, may be used. Optimum temperatures for growth are between 20 - 35°C. pH ranges as high as 10 have been used but optimum growth is observed between pH 7.5 and 9.0. Most of the suitable bacteria identified to date are aerobic, heterotrophic, and slow growing. Hence, washout or takeover by other organisms are primary concerns in the selection of a suitable biological reactor; a fixed film process is strongly recommended to ensure the retention of the biomass in the system.

Biological treatment processes, reported to remove cyanide from industrial wastewaters include:

i) trickling filters (synthetic and metal plating wastewaters),
ii) activated sludge (synthetic, coal gasification and coke oven wastewaters),
iii) extended aeration (synthetic feeds),
iv) activated sludge with powdered activated carbon addition (coke oven wastewaters),
v) immobilized enzymes (synthetic wastewaters),
vi) rotating biological contactors (coke oven and gold milling wastewaters).

All attached growth processes are capable of yielding good to high quality, low toxicity effluents but the rotating biological contactor was selected as the process of choice owing to its cost effective design and low operating costs.

In activated sludge and extended aeration systems stripping is the major removal mechanism which accounts for 60 - 80% of the cyanide removed. Biological metabolism ranks second in importance, and is responsible for 20 - 40% of the cyanide removed. Adsorption and chemical reaction with substrates remove less than 15% of the cyanide. Some investigators have observed that biological metabolism predominates below cyanide concentrations of 40 - 60 mg/L. The predominant removal mechanisms in other biological treatment systems are not well known.

RECOMMENDATIONS

i) Biodegradation studies should be carried out with gold mill or silver mill cyanide bearing wastewaters.

ii) A fixed film process is strongly recommended. The rotating biological contactor, demonstrated by Homestake Gold Mines, appears to be a good candidate for further studies.

iii) Locally collected microfauna at various gold milling sites should be tested for cyanide removal ability.

iv) Methods of recovering a greater portion of the cyanide from the barren stream should be investigated.

v) Sources of warm water process streams should be located for a deep gold mine. An evaluation should be conducted to determine the feasibility of using these streams for heating value in order to maintain sufficient bioreactor temperatures.

ABRÉGÉ TECHNIQUE

Une revue de la littérature a été entreprise pour déterminer si les procédés de traitement biologique peuvent profiter à l'industrie de traitement des minerais du Canada, dans le cas des eaux usées contenant du cyanure. L'étude a été réalisée en deux étapes. Tout d'abord, les informations portant sur les procédés biologiques utilisés pour le traitement des eaux usées cyanurées, ont été compilées et résumées sous forme d'un rapport provisoire. La deuxième étape du processus d'évaluation a consisté en une revue critique des procédés dégagés au cours de la première étape, afin de choisir celui qui servira aux études de biodégradation.

On a souligné aussi les points où l'information est insuffisante et qui nécessitent donc d'autres recherches avant l'application pratique du procédé proposé. Le rapport final résume les résultats des deux étapes.

La biodégradabilité du cyanure est influencée par de nombreux facteurs, en particulier:

i) Les caractéristiques chimiques des écoulements d'eaux usées à traiter (niveaux de cyanure, type de composé au cyanure, concentration en métaux lourds, variabilité, concentrations d'autres espèces chimiques).

ii) Les caractéristiques des micro-organismes(vitesse de croissance, besoins en substances nutritives, concentrations tolérables en cyanure, vitesse d'absorption du cyanure, type de cyanure dégradable, pH optimum et gammes des températures pour la croissance, inhibiteurs).

iii) Les caractéristiques du procédé (débits de déversement autorisés, sensibilité aux déchargements massifs, destinée du cyanure dans le système, pouvoir de décantation des boues, disponibilité des substances nutritives et de l'oxygène, contrôle de la biomasse).

Lors de l'étude de la littérature, une attention toute particulière a été accordée à ces détails, qui ont servi ensuite à l'examen comparatif des différents types d'eaux usées et de procédés biologiques.

L'étude a porté ensuite sur les effluents suivants, contenant du cyanure, et rejetés par cinq installations de traitement de minerais:

- Écoulements stériles des usines de traitement de l'or, rejets liquides de désintégration et des bassins de retenue des résidus d'épuration
- Déchets liquides des usines de traitement de l'argent
- Liquides résiduaires surnageant, contenant des sulfures de métaux communs
- Sous-produits résiduaires en provenance de la purge de cokerie et des hauts fourneaux, lors de la production de fer
- Déchets liquides rejetés après lessivage du chemisage des cuves d'électrolyse utilisées dans la production d'aluminium à partir de la bauxite.

Le facteur le plus important dans la détermination de la biodégradabilité du cyanure dans un type donné d'eaux usées, est la stabilité thermodynamique de la forme prédominante sous laquelle se trouvent les complexes de cyanure en solution. Les complexes très stables cyanure-métal, comme avec le fer et le cobalt, ne sont pas dégradés facilement par des organismes vivants. Ils sont cependant moins toxiques que les complexes à liaison faible. On rapporte qu'ils ont franchi des systèmes de traitement biologique sans effets inhibiteurs. Les complexes au

cyanure qui sont modérément stables, ne sont qu'en partie biodégradés. Les ions cyanure libres sont biodégradables à 100%. Ces données ont permis d'étudier les possibilités de traitement des eaux usées contenant du cyanure.

Les eaux résiduaires qui nécessitent une recherche plus poussée sont celles rejetées par les usines de traitement de l'or et de l'argent. Le traitement biologique des déchets liquides des industries de la métallurgie du fer et de l'acier est bien au point; il n'est donc pas nécessaire de poursuivre les recherches plus en détail. Les complexes cyanure-fer à liaisons solides prédominent dans les rejets d'épuration des mines de métaux communs et dans les effluents de lavage issus de la fabrication d'aluminium. Ces déchets liquides n'ont par conséquent pas été choisis pour les études de biodégradation.

Les bactéries qui métabolisent les complexes cyanure-métal à faible liaison, ont été identifiées (voir tableau 7.1.1.). Il est possible d'utiliser les souches microbiennes de la flore prélevée localement ou l'un des nombreux micro-organismes connus pour leur faculté à dégrader le cyanure. Les températures optimales de croissance sont situées entre 20 et 35°C. Des valeurs de pH de 10 ont été utilisées, mais la croissance optimale est observée pour un pH situé entre 7,5 et 9. La plupart des bactéries appropriées et reconnues jusqu'à présent sont aérobies, hétérotrophes et à croissance lente. D'où il découle qu'un lavage ou l'avantage que prendraient d'autres organismes représentent des problèmes de première importance dans le choix d'un agent biologique approprié. Il est fortement recommandé d'utiliser un procédé à film immobile pour assurer la rétention de la biomasse dans le système.

Les procédés de traitement biologique utilisés pour extraire les cyanures des déchets liquides industriels comprennent:

i) les lits bactériens (eaux résiduaires des usines de placage métallique et de matières plastiques),

ii) les boues activées (eaux résiduaires des usines de matières plastiques, de gazéification au charbon et des cokeries),

iii) l'aération prolongée (rejets des usines de matières plastiques),

iv) les boues activées avec addition de charbon actif en poudre (eaux résiduaires des cokeries),

v) les enzymes immobilisés (eaux résiduaires des usines de matières plastiques),

vi) les mélangeurs biologiques rotatifs (eaux résiduaires des cokeries et usines de traitement de l'or).

Tous les procédés de croissance des micro-organismes par fixation produisent des effluents peu toxiques, classés de bon à très bon. Le mélangeur biologique rotatif a été choisi en raison du faible rapport coût de l'installation/performances et des faibles coûts d'exploitation.

Dans les procédés aux boues activées et en aération prolongée, le raclage constitue le principal mécanisme d'enlèvement du cyanure, environ 60 à 80%. Le métabolisme biologique se classe au deuxième rang, en enlevant 20 à 40% du cyanure. L'adsorption et les réactions chimiques avec substrats enlèvent 15% du cyanure. Quelques chercheurs ont observé que le métabolisme biologique prédomine pour des concentrations de cyanure inférieures à 40 - 60 mg/L. Les mécanismes d'épuration prédominants des autres systèmes de traitement biologique ne sont pas bien connus.

RECOMMANDATIONS

i) Des études de biodégradation devraient être menées pour les déchets liquides cyanurés issus des usines de traitement de l'or ou de l'argent.

ii) Le procédé à film immobile est fortement recommandé. Un bon choix pour mener d'autres études, semble être le mélangeur biologique rotatif présenté par Homestake Gold Mines.

iii) La capacité d'épuration du cyanure par la microfaune prélevée sur place à différentes usines de traitement de l'or, devrait faire l'objet de tests.

iv) Des recherches devraient être menées pour trouver des méthodes permettant de récupérer une plus grande proportion du cyanure dans les écoulements stériles.

v) Il faudrait localiser des sources d'eau chaude pour les mines d'or profondes. Une étude devrait être menée pour déterminer s'il est possible d'utiliser ces eaux pour maintenir la réaction biologique à des températures suffisantes.

1.0 INTRODUCTION

A literature review was undertaken to assess the applicability of biological treatment for cyanide bearing effluents from Canadian mineral processing industries. To assist in the selection of suitable biological treatment methods, the characteristics of cyanide bearing effluents from mineral processing plants were reviewed, the types of organisms capable of degrading cyanide were identified, and the cyanide removal mechanisms were established. Various biological treatment processes were reviewed and compared. Experience gained in the biological treatment of cyanide bearing wastewaters produced by non-mining industries, can be extended to the treatment of wastewater streams from mineral processors. Therefore, a discussion of the relevant experience of other industries is also presented.

The principal industries producing cyanide bearing wastewaters are:

* Precious metals mills (extraction of silver and gold)
* Mineral dressing (pyrrhotite and base metal flotation)
* Primary iron and steel manufacturing (scrubber waters from blast furnaces and weak ammonia liquor from coke oven byproduct recovery plants)
* The primary aluminum manufacturing (leach liquors from spent pot-linings)
* The metal plating industry
* The photographic industry
* The petrochemical industry
* The coal gasification industry

Only the first four industries listed above, are engaged in mineral processing. Effluents from these industries contain, in addition to cyanide (free and complexed with heavy metals), variable amounts of thiocyanate, flotation agents, ammonia and organics. The principal metals present at various concentrations are copper, nickel, iron, zinc, arsenic and cadmium.

Soluble cyanide concentrations as low as 1 ppm have been shown to be toxic to microflora and microfauna comprising the food chain of fish and other animals. In the U.S., the Environmental Protection Agency has enacted strict regulations to control the amount of soluble cyanide which may be discharged from any source into natural waters; soluble cyanide concentrations are limited to less than 0.02 ppm of cyanide in the wastewater. Similar regulations are expected in Canada. Such regulations create problems for industries such as mining which have traditionally relied upon dilution to reduce the free cyanide concentration of waste streams.

Over the past five to six years, physical/chemical methods, in particular, alkaline chlorination and the Inco SO_2 process, have been implemented as alternative treatment methods to natural degradation in tailings ponds at some gold mines (Scott, 1984). However, chemical costs are exceptionally high. For example, a 5000 ton per day gold mine will spend one million dollars a year for the alkaline chlorination treatment of barren bleed (Hawley, 1984). Furthermore, ferrocyanide is not decomposed, toxic chlorine derivatives may be formed and in some cases effluent quality is not acceptable (Mudder and Whitlock,1983). The Inco SO_2 process is less expensive than alkaline chlorination. However, the treated effluent

is high in cyanates - a less toxic but undesirable species. A need exists for a reliable and cost effective treatment process that will ensure the virtually complete, elimination of cyanide without transferring the problem to other media.

Traditionally, biological treatment has been applied to cyanide bearing wastewaters containing organic substances (coke-plant effluents, wastewater from petrochemical plants, synthesis of organic chemicals, etc.). Physico-chemical treatment, on the other hand, has been mainly suggested for cyanide bearing wastewaters containing heavy metals such as those produced by metal plating industries and gold mines. The reason for this was a documented resistance to biological decompositon of several metal-cyanide complexes and a generally inhibitory/toxic influence of heavy metals on biological treatment. The successful pilot plant investigations of Mudder and Whitlock (1983) at Homestake Gold Mines, using a rotating biological contactor (RBC), indicate that biological treatment is a viable alternative for cyanide bearing wastewaters containing heavy metals. However, site specific characteristics (ie. effluent composition, local climatic conditions) may preclude the use of this technology at other locations.

To enable the evaluation of biological processes for the degradation of cyanide wastewaters, the report is organized into seven major areas. First, cyanide bearing streams for the major mineral processors are identified. Second, the characteristics and toxicity of these streams are discussed. Third, the types of organisms which may be useful in a biological treatment process are summarized. The metabolic pathways of degradation are also given. Fourth, biological

processes which have been studied for the degradation of simple and complexed cyanides are summarized; in this section the treatment concept used at Homestake Gold Mines is critically reviewed. The limitations of biological treatment are also given. Fifth, a candidate process is selected for biodegradation studies. Next the chemical pretreatment and post-treatment methods are presented and discussed since physical/chemical methods are a necessary consideration in any complete treatment system. Finally, the major conclusions of the literature review are presented and the research needs are identified.

2.0 OBJECTIVES

The objectives of this project are:

i) To prepare a critical state-of-the-art review of the biological processes available for the destruction of cyanide in mineral processing effluents. Particular emphasis will be given to the Homestake Mining Company process.

ii) To evaluate these processes, and select those which may be potentially suitable to Canadian mineral processing operations based on a review of critical parameters, capital and operating costs, and legal aspects.

iii) To identify information gaps and research needs necessary prior to industrial application.

2.1 Approach Taken

The work program was organized by Tasks as summarized with their corresponding outputs in Table 2.1. Tasks #1 and #2 constitute Milestone 1 and Tasks #3 and #4 make up Milestone 2. The output of all tasks are summarized in the final report in accordance with the specifications of DSS File No. 15SQ.23440-4-9184.

The project background information on the biological destruction of cyanide effluents was compiled through a computerized literature review, telephone contacts with appropriate researchers (Alcan Research Centre, Kingston), mining companies (Noranda), and government agencies. Direct contact was made with Homestake Mining Company. However, permission for a site visit, to obtain further details on their operating experience to-date, was refused by Homestake. The review was completed with data available in the

TABLE 2.1

PROJECT TASKS AND OUTPUT

Task No. and Title	Output
Task #1 - Literature Review and Information Assembly	Summary of computer assisted and manual literature search of all biological treatment processes applicable to mineral processing effluents. Direct contacts with appropriate researchers, industries, and government agencies. Direct contact with Homestake Mining Company, Lead, South Dakota.
Task #2 - Evaluation and Selection of Potential Biological Process (es)	Classification and tabulation of data. Comparison and critical evaluation of current or potential biological treatments of cyanide effluents. A selection and detailed review of one or more processes applicable to the Caadian industry, including a review of: 1. Critical parameters for biological destruction. 2. Capital and operating cost estimate. 3. Legal aspects.
Milestone #1	Draft report of tasks #1 and #2
Task #3 - Identification of Research Needs	Based on the above review, information gaps and research needed prior to practical application of the proposed process will be identified, presented and discussed.
Task #4 - Final Report Preparation (Milestone #2)	A detailed report summarizing the activities and results of all above tasks.

published literature. Visits were made to government offices and laboratories including Environment Canada's Wastewater Technology Center in Burlington and the Ministry of Environment in Toronto, to collect information on the characteristics of mining industry wastes, and regulatory effluent requirements.

The RBC process was evaluated in detail and critically compared with other biological systems in terms of critical process parameters and economic considerations. Capital and operating costs, recovery of values, and legal considerations were also examined in detail for the RBC process.

The characteristics and requirements of cyanide bearing effluents from Canadian mineral processing operations were reviewed and coupled to the most appropriate promising biological process.

An outline of considered topics in Milestone 1 are given below:

- Characteristics of cyanide bearing mineral processing effluents.
- Canadian regulations governing cyanide bearing mining effluents.
- Identification of the types of micro-organisms involved.
- Identification of the mechanisms of cyanide removal in biological treatment processes.
- Determination of the type of cyanide degradable.
- Critical review of biological processes developed and tested to date (including the Homestake RBC Process).
- Identification of critical process design and operational parameters.

- Identification of special problem areas (eg. adaptation of microorganisms, operating temperatures, variablility of effluent stream compositions, chronic metal toxicity, etc.).

This information was used in Task #2 to select candidate biological processes for further investigation.

3.0 SOURCES OF CYANIDE IN THE MINERAL PROCESSING INDUSTRY

The principal consumer of cyanide is the mineral processing industry which, in 1978, used sixty seven per cent of the total cyanide sold in Canada (refer to Table 3.1). Cyanide is primarily used at gold/silver mines and base metal sulfide mines using froth flotation circuits (Huiatt, 1984, Huiatt et al., 1983). Major Canadian mines and milling operations using cyanide are listed in Table 3.2.

TABLE 3.1

CONSUMPTION RATES OF CYANIDE IN CANADA (1978)

Cyanide Consumption (tons/year)	Industry	Percent of Total
2700	Gold	56 %
500	Mining, other than gold	11 %
1600	Non-mining, industrial	33%
4800	All industries	100%

Source: Ingles and Scott, 1981.

Although the primary iron and steel, and the aluminum manufacturing industries do not use cyanide in their processing circuits, cyanide is produced as a by-product of their operations. Mineral processing industries, producing cyanide bearing wastewater streams, are briefly reviewed in the next five subsections.

TABLE 3.2

CANADIAN MINE AND MILLING OPERATIONS USING CYANIDE

Mine	Daily Tonnage of Ore Processed	Mine	Daily Tonnage of Ore Processed
Agnico-Eagle Mines Joutel, PQ	1,200	Giant Yellowknife Mines Yellowknife, NWT	1,250
Belmoral Mines Val d'Or, PQ	1,100	Kerr-Addison Mines McGary, Ont.	1,300
Camflo Mines Malartic, PQ	1,290	Kiena Gold Mines Val d'Or, PQ	1,200
Campbell Red Lake Balmertown, Ont.	1,075	LAC-La Mine Doyon Rouyn, PQ	3,000
Carolin Mines Larder Creek, BC	1,500	LAC-Bousquet Mine Malartic, PQ	1,500
Detour Lake Mines Timmins, Ont.	2,500	Pamour Porcupine Timmins, Ont.	4,400
Dome Mines S. Porcupine, Ont.	1,985	Sigma Mines Val d'Or, PQ	1,400
Echo Bay Mines Lupin, NWT	1,200	Teck-Corona Div. Val d'Or, PQ	2,100
East Malartic Mines Malartic, PQ	1,850	Canadian Tungsten Tungsten, B.C.	1,000

Mine information is from the "Canadian Mines Handbook" 1984-85 and "Mining and Milling in Canada", an EMR Canada Report 1983.

NOTES:

1. This list only includes major producers of >1,000 tpd. During 1985-86, three large gold operations will open in Hemlo Ontario (Noranda, Teck-Coruna and LAC).

2. Four of the seventeen gold mines listed above use the C-I-P process.

3.1 Processing of Gold Bearing Ores

There are many variations in gold processing circuits. Of these, two processes are primarily used by Canadian gold mills. The following steps are involved:

1) Grinding, cyanidation, liquid-solids-separation, clarification, deaeration, zinc precipitation (Merril-Crowe process) and smelting.
2) Grinding, cyanidation, carbon-in-pulp adsorption, stripping of carbon and electrowinning.

The Merril-Crowe zinc precipitation route is used by thirty of the thirty-six major gold mines in Canada (Scott, 1984a; Zaidi, 1985). A flow diagram of a simplified flotation-cyanidation gold extraction circuit is given in Figure 3.1 (Zaidi, 1985). Typical consumption rates of chemicals, used in the extraction of gold, are listed in Table 3.3.

After primary flotation, the concentrate is treated with lime and sodium (or calcium) cyanide. The resulting mixture is contacted in a series of countercurrent decantation cells, where the majority of the gold dissolves by the reaction (Huiatt et al.,1983):

$$2\ Au + 4\ CN^- + O_2 + 2\ H_2O \longrightarrow 2\ Au(CN)_2^- + H_2O_2 + 2\ OH^-$$

A small but significant proportion dissolves via the Elsner's equation:

$$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \longrightarrow 4\ Au(CN)_2^- + 4\ OH^-$$

FIGURE 3.1

SCHEMATIC FLOW SHEET FOR THE MERRIL-CROWE PROCESS
(Zaidi, 1985)

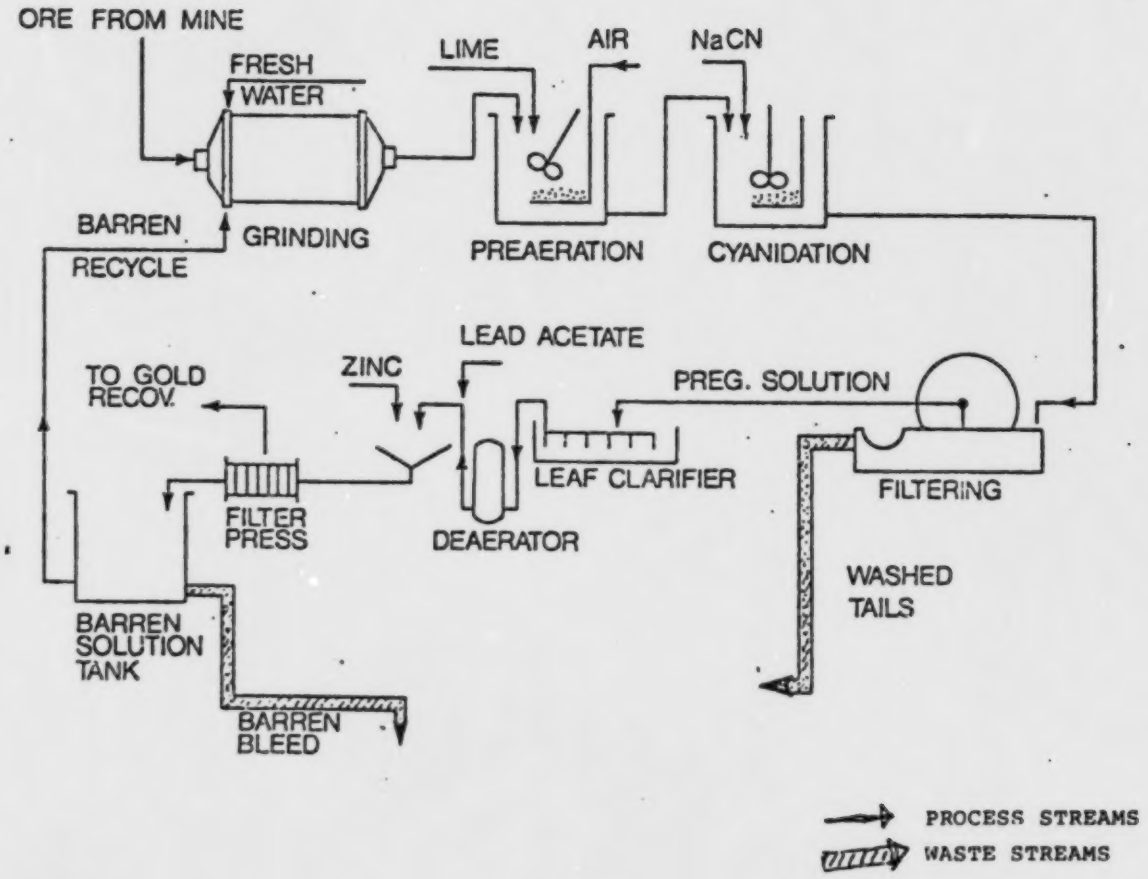


TABLE 3.3

SUMMARY OF REAGENT USAGE IN GOLD MINES

MINE & REAGENT USAGE lb/TON ORE

Reagent	1	2	3	4	5	6	7	8	9	10	11	12	13
Sodium Cyanide	1.565	NA	0.309	2.424	0.234	0	1.26	2.18	0.40	0.73	0	0.298	1.3
Potassium Cyanide	-	-	-	-	-	0.75	-	-	-	0.507	0	0	0
Xanthate	0.213	-	-	0.1015	0.096	0.258	-	0.36	-	0	0	0	0
Frothers	0.058	-	-	-	0.058	0.0136	-	0.06	-	0	0	0	0
Kerosene	-	-	-	0.005	-	-	-	0.60	-	0	0	0	0
Lead Nitrate	-	-	0.0086	-	0.015	0.0037	-	0.008	0.007	-	0	0	0
Lead Acetate	-	-	-	0.0385	-	-	-	0	0.001	0.007	0	0.002	0.01
Zinc Dust	0.103	-	0.0267	0.2007	0.093	0.0204	0.15	0.08	0.026	0.069	0.02	0.04	0.11
Lime	1.619	-	-	3.117	3.89	1.03	7.30	-	2.70	0.950	3.5	1.59	1.31
Litharge	0.20	-	-	-	-	-	-	-	0	0	0	0.050	0
NH_4Cl	0	-	0	0	0	0	0	0.002	0	0	0	-	0
Aero Cyanide											0.45	-	0

Lime is added to keep the system at an alkaline pH of 10-11. This stream eventually becomes rich in gold and is then termed the pregnant solution. The gold is recovered by precipitation with zinc dust as represented by the equations below (Brickell, 1981). The gold is recovered from the precipitate and finally, refined in a bullion furnace.

$$Zn + NaAu(CN)_2 + H_2O + 2\ NaCN \text{ -------> } Na_2Zn(CN)_4 + Au + NaOH + 1/2\ H_2$$

$$Zn + 4\ NaCN + 2\ H_2O \text{ -------> } Na_2Zn(CN)_4 + 2\ NaOH + H_2$$

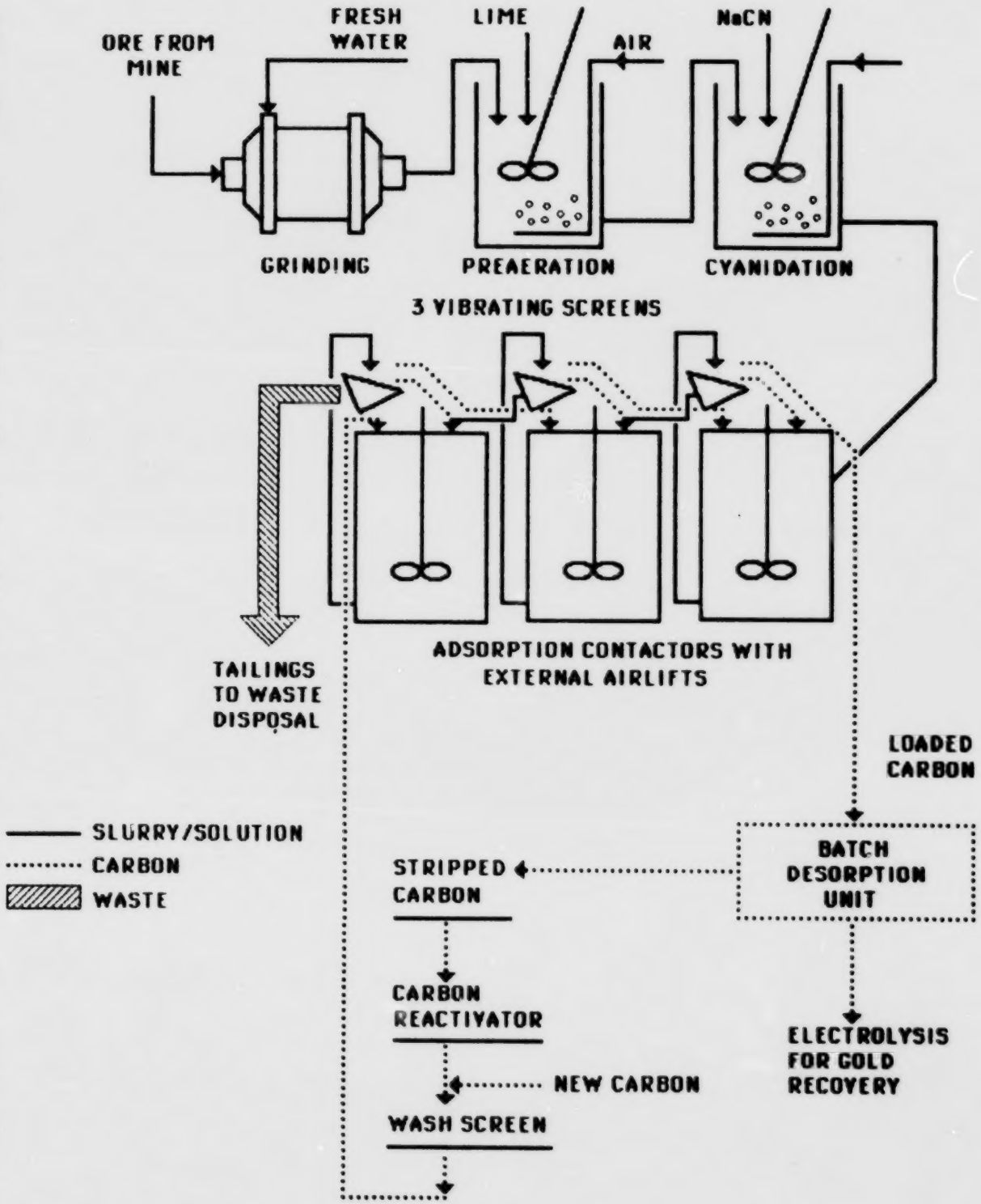
$$2\ Zn + 8\ NaCN + O_2 + 2\ H_2O \text{ -------> } 2\ Na_2Zn(CN)_4 + 4\ NaOH$$

The preceeding equations show that zinc not only precipitates gold but also consumes cyanide. In order to avoid deleterious build up of zinc and other metal impurities, a portion (approximately 50%) of the "gold-free" or barren solution must be discharged from the mill. In addition to free cyanide, the principal constituents of the barren solution are the simple cyanides of sodium (or calcium) and the cyanide complexes of copper, iron (less frequently), nickel, zinc, thiocyanates, silica, and, at some mines arsenic. In some mills, the filter cake is given an additional water wash to reduce the cyanide in the water with the solids before they are pumped to the tailings impoundment area. Thus, the conventional gold mill produces two principal cyanide containing waste streams -- the waste barren solution and the tailings slurry. Since a major portion of the barren solution is wasted, a research need of any proposed pollution abatement program is the recovery and recycle of cyanide from the barren.

Six of the thirty-six major gold mines in Canada use the carbon-in-pulp (CIP) route (refer to Figure 3.2). This process involves the use of activated carbon for the treatment of pulps containing dissolved precious metals and provides an alternative to the conventional gold recovery process using filtration or counter-current decantation in conjunction with the Merril-Crowe zinc precipitation process. Following cyanidation, no attempt is made to separate and recycle the cyanide solution. The gold is recovered from solution by adsorption of the gold cyanide complex on activated carbon in a series of countercurrent adsorption contactors. The separation of the pulp and carbon for transfer from stage to stage is based on size difference and is achieved by interstage screening. The barren pulp is generally disposed of as tailings. The loaded carbon is washed before transfer to the elution section, where the gold is stripped from the carbon using a solution of 0.1% NaCN and 1.0% NaOH. Operating temperatures and pressures are 85-160°C and 50-100 kPa, respectively; the conditions depend upon which one of four stripping techniques is selected (Dahya and King, 1983). The metallic gold is recovered from the pregnant stripping solution by electrowinning. When a cathode is loaded with the required amount of gold, it is removed from the cell and smelted with a flux to produce high purity bullion. A portion of the barren stripping solution is combined with the barren pulp slurry and sent to the tailings pond.

Use of zinc precipitation is more complicated than electrowinning as there has to be equipment for solution clarification and deaeration, zinc addition, precipitate filtration and drying. When dealing with large throughputs of low-grade ores, the capital and

FIGURE 3.2
SCHEMATIC FLOWSHEET FOR THE CARBON-IN-PULP PROCESS
(ZAIDI et al , 1985)



operating cost of liquid-solid separation is significant in relation to the total cost. This is particularily true in countries like Canada, where, because of the climate, it is necessary to enclose all equipment and to insulate and heat buildings. Although, fewer plants are using the CIP process at the present time, this technology will clearly be the dominant method of gold extraction in new installations.

3.2 Processing of Silver Bearing Ores

Silver can be extracted from its ore by techniques similar to those used in the recovery of gold. Following cyanidation,

$$4\ Ag + 8\ NaCN + O_2 + 2\ H_2O \text{ ---------> } 4\ NaAg(CN)_2 + 4\ NaOH$$

the silver is precipitated by zinc dust or aluminum powder. This method is not economic for low grade silver ores; hence, Equity Mines (B.C.) is the only silver mine using cyanidation in Canada. The process effluents are relatively richer in cyanides than those used in gold processing because higher concentrations of cyanide are needed to dissolve the silver from the ore.

3.3 Flotation of Base Metal Sulfide Ores

In the recovery of minerals or metals from ores, the usual procedure is to physically separate the desired minerals from the waste or gangue minerals. To accomplish this, the ore must be crushed and ground finely enough to liberate the minerals so that they can be separated from each other on the basis of differences in their

physical or chemical properties. The most commonly used method of carrying out mineral separation is flotation, which utilizes differences in the hydrophobicity of minerals to separate them. In almost all cases, minerals must be made selectively hydrophobic through the addition of organic surface-active chemicals called collectors. To achieve the desired selectivity, other reagents may be added to modulate the role of the collector. Those reagents which are added to cause a collector to adsorb on the mineral surface are called activators. Other reagents are added to prevent the adsorption of the collector; these reagents are called depressants. In the flotation of base metal sulfide ores, cyanide is often added as a depressant. Base metal mines using cyanide are listed in Table 3.4.

In lead-zinc separation, cyanide is added to prevent the activation of sphalerite while galena is being floated. Similarly, cyanide is used to prevent sphalerite flotation in copper-zinc mineral separations. In copper-lead separations, copper minerals are depressed with cyanide complex. In copper-molybdenum separations, chalcocite is depressed with ferrocyanide and cyanide. In copper-iron separations, pyrite depression is achieved at high pH through cyanide additions. The principal cyanide-bearing waste from froth flotation processing is the final tailings slurry.

3.4 Origins of Cyanide During the Production of Iron and Steel

The iron and steel industry cyanide wastes are mainly generated from:

i) Blast furnace gas scrubber and cooling waters, which are of large volume and low cyanide concentrations.

TABLE 3.4

BASE METAL MINES USING CYANIDE

Company	Products	Daily Tonnage of Ore Produced (tons/day)	Cyanide Consumption (lb NaCN/ton)	Date
Brenda Mines Ltd*	Cu, Mo	30,000	0.007	Sept '82
Cominco Ltd. Sullivan	Pb, Zn	7,000	0.09	Oct '83
Falconbridge Ltd. Strathcona	Cu, Ni	6,500	0.01	Feb '82
Hudson Bay Mining & Smelting	Cu, Pb, Zn	3,400	0.05	Jan '85
Inco Copper Cliff	Cu	10,000	0.25	-
Kid Creek Mines Ltd.	Cu, Pb, Zn	12,000	0.1	Feb '82
Mattabi Mines Ltd.	Cu, Pb, Zn	2,600	0.015	Feb '85
Noranda Mines Ltd. Geco	Cu, Pb, Zn	5,000	0.25	Feb '85
Tech Corp Logan Lake	Cu	28,000	0.025	April '84
Utah International Inc. Island Copper	Cu, Mo	1,000	0.2**	-
Westmin Resources Ltd. Campbell River	Cu, Pb, Zn	900 3,000***	0.3	-

* may not still be operating
** Molybdenum circuit only
*** capacity increasing to this value in 1985

Cyanide usage in base metal flotation processes is approximately 0.02 kg/tonne

ii) Coke oven by-product recovery operations that produce, relatively high-concentration cyanide wastes. These wastes are a mixture of free, simple, and complex cyanides.

During the destructive distillation of metallurgical coal to form blast furnace coke, coal volatiles (carbon monoxide, hydrogen and carbon dioxide) and moisture are produced. Tars, phenols, and other organic and inorganic components are also released as impurities. The cooling and cleaning of these gases results in weak ammonia liquor (WAL), which contains organic and inorganic compounds, simple and substituted phenols, polyhydric phenols, ammonium hydroxide, and the ammonium compounds of sulfide, chloride, sulfate, thiosulfate, thiocyanate, and cyanide. The concentrations of these contaminants are functions of coking temperatures and of the coking coals used.

3.5 Origins of Cyanide During the Production of Aluminum

Both cryolite-alumina melt and the liquid aluminium are extremely corrosive materials. For this reason the steel cathodes used in the electroytic cells are lined with carbon (see Figure 3.3). The lining consists of calcined anthracite with a pitch binder. However, physical and chemical processes occur in the cathode lining with time:

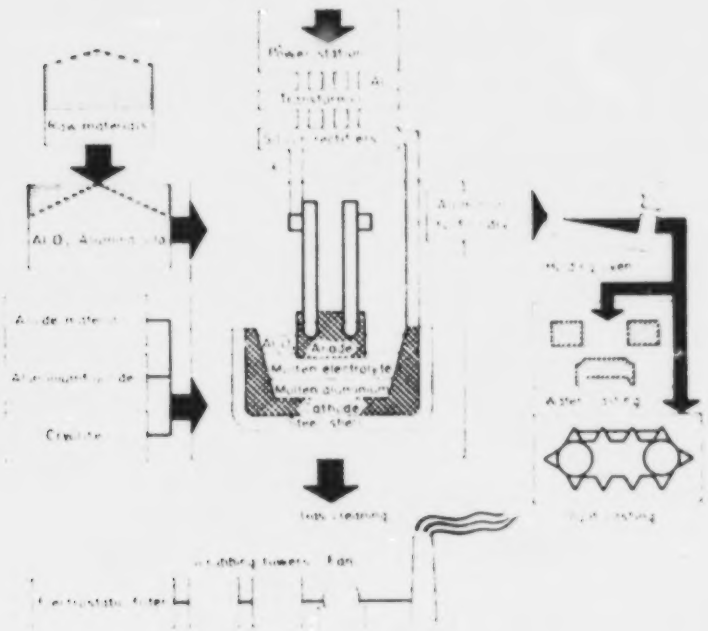
a) Carbide formation

b) Melt penetration

c) Sodium uptake

d) Sodium-electrolyte reaction

Figure 3.3 Flow-sheet for aluminium production from alumina.
(Taken from Grjotheim and Welch, 1980)



If these factors are not closely monitored a catastrophic failure of the cell may follow. The basic signs for the need to replace cathode linings (i.e. iron contamination or high cell voltage) can often be traced back to fracturing of the carbon and growth of massive crystals of fluorides. Normally cells are relined after 1200 to 1600 days of operation. The leach-liquor from weathered stockpiles of failed cathode lining material will contain some sodium cyanide (Grjotheim and Welch, 1980). Earlier it was assumed that this arose from weathering reactions involving sodium, the nitrogen in air and aluminium carbide. More recently it has been detected in fresh samples of failed cathodes and in zones remote from the aluminium carbide. This suggests that the reaction:

$$2\ Na\ (bath) + 2\ C\ (lining) + N_2(air) = 2\ NaCN$$

is ongoing during electrolysis. This process is thermochemically favoured at the temperatures involved and is catalysed by iron compounds. Other compounds found in cathode linings are aluminium nitride and sodium fluoride. Upon alkaline hydrolysis the former gives rise to ammonia which is usually noticed in freshly removed cathode linings. The aluminium nitride can also contribute to the formation of sodium cyanide when there is a continuing source of sodium and air. Formation of iron compounds have also been indicated from examinations of the steel collector bars which often display signs of alkali from the electrolyte. The latter would also explain iron contamination of the electrolyte.

The wastewater streams from the five mineral processing industries are characterized in the next section.

4.0 GENERAL CHARACTERISTICS OF CYANIDE BEARING MINERAL PROCESSING EFFLUENTS

4.1 Gold Mill Effluents

Barren bleed and repulped tailings slurry were identified in section 3.1 as the major cyanide bearing streams from the Merril-Crowe zinc precipitation process. Barren pulp slurry, is the only cyanide bearing stream from the carbon-in-pulp process. Analyses of these effluent streams, for several Canadian gold mines, are given in Tables A1-A14 of Appendix A.

Cyanide removal/destruction processes may be applied to selected process waste streams or to the combined wastes. The alternative treatment schemes for gold mill effluents are presented in Figure 4.1 (Zaidi et al. 1985). At some gold mills more than one pond is used to enable separate treatment of the barren bleed or to enable further polishing of the tailings pond overflow.

Cyanide complexes that exist in gold-milling solutions were classified as follows by Ingles and Scott (1981):

a) Free Cyanide CN^-, HCN

b) Simple Compounds

   i) readily soluble NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$

   ii) relatively insoluble $Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$, AgCN

c) Weak Complexes $Zn(CN)_4^{2-}$, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$

d) Moderately Strong Complexes $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$

e) Strong Complexes $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$

Free cyanide (CN_F) refers to a summation of CN^- ion and molecular HCN. Weak-acid-dissociable cyanide (CN_W) refers to all cyanide forms except the most stable cyanide complexes such as those

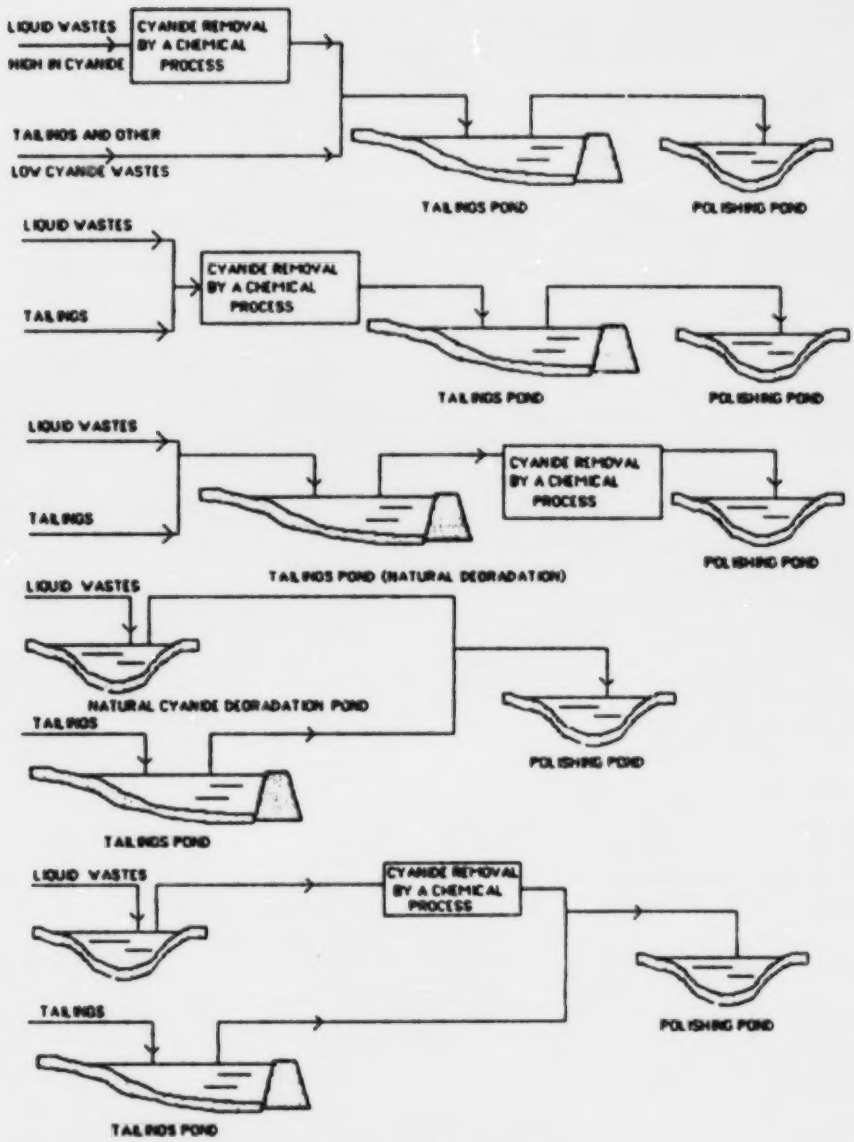


FIGURE 4.1 FIVE ALTERNATIVE SCHEMES FOR COMBINING OR SEGREGATING THE WASTE STREAMS FROM A GOLD MINE TO MINIMIZE EFFLUENT TREATMENT COSTS (ZADRA ET AL., 1985)

of iron, cobalt and gold. Total cyanide (CN_T) refers to all cyanide forms including iron cyanide but excludes cobalt and gold cyanides. In addition, gold mill effluents contain thiocyanate (SCN^-). Cyanate (CNO^-) is present in gold mill effluents treated using the Inco SO_2 process.

In general, the stronger the complex, the less free cyanide ion concentration is required to maintain it in solution, and conversely, the less readily it yields cyanide ion as the excess is reduced by acidification or destruction reactions. In a solution of a metal complex cyanide, the proportion of the metal and cyanide combined in the complex ion can be calculated from the instability constant, if the pH value of the solution is known. Results of such calculations, at pH 7.5, were presented by Pettet and Mills (1954) and are reproduced in Table 4.1. It can be seen that, in a dilute solution containing 1 ppm of cyanide, the complexes of zinc and cadmium are almost completely dissociated, whereas, at 100 ppm and 200 ppm of cyanide, appreciable proportions of complex ion are formed.

Many candidate biological treatment processes require influent cyanide concentrations less than 200 ppm. Barren bleeds contain total cyanide levels of 40-750 ppm. Thus, chemical pretreatment or dilution with mine water or tailings pond overflow is required. Cyanide concentrations of tailings repulp streams (13-280 ppm) and tailings pond overflow are within the range of interest for biological treatment.

Flow rates of the cyanide bearing wastewater streams, the fraction of free cyanides present in these process streams, and their respective SCN^-/CN^- ratios, are given in Tables 4.2A-D for six gold

TABLE 4.1

CALCULATED CONCENTRATIONS OF CYANIDE AND METAL COMBINED IN METALLOCYANIDE IONS IN SOLUTIONS OF pH 7.5

Complex ion	Value of instability constant used	Cyanide (as HCN, ppm)			Metal, ppm	
		Total	Combined in complex ion	Uncombined	Combined in complex ion	Uncombined
$Cd(CN)_4^{2-}$	5×10^{-20}	1	1.4×10^{-6}	1.00	1.5×10^{-6}	1.04
		10	0.14	9.8	0.14	10.3
		100	66.1	33.7	68.9	35.6
		200	161	39	167	41
$Zn(CN)_4^{2-}$	2.47×10^{-20}	1	2.9×10^{-6}	1.00	1.8×10^{-6}	0.61
		10	0.26	9.7	0.16	5.9
		100	70.1	29.9	42.5	18.3
		200	166	34	101	21
$Cu(CN)_3^{2-}$	5×10^{-28}	1	0.99	0.007	0.78	0.006
		10	9.99	0.013	7.85	0.010
		100	99.98	0.023	78.48	0.019
		200	199.97	0.27	156.98	0.022

SOURCE : Pettet and Mills (1954)

TABLE 4.2

FLOW RATES AND CHARACTERISTICS OF CYANIDE BEARING GOLD MILL EFFLUENTS

TABLE "A"
BARREN BLEED STREAM
QUEBEC

MINE	FLOW IPGM	CNT	SCN	CNF/CNT	SCN/CNT
QA	28.4	610	400	0.836	0.656
QB	22.6	220	180	1.000	0.818
QC	6	300	54	0.967	0.180
QD	85	86	42	0.977	0.488
QE	41.7	120	200	1.000	1.667

TABLE "B"
REPULPED TAILINGS STREAM
QUEBEC

MINE	FLOW IPGM	CNT	SCN	CNF/CNT	SCN/CNT
QA	29.2	160	120	0.938	0.750
QB	135.4	33	24	0.970	0.727
QC	358.3	97	18	0.928	0.186
QD	256.9	41	16	0.659	0.390
QE	78.8	85	74	0.824	0.871

TABLE "C"
MINE WATER COMPOSITION
QUEBEC

MINE	FLOW IPGM	CNT	SCN	CNF/CNT	SCN/CNT
QA	171	0.19	N/A	N/A	N/A
QB	160	0.06	N/A	N/A	N/A
QC	243	0.07	N/A	N/A	N/A
QD	183	0.12	N/A	N/A	N/A
QE	174	0.12	N/A	N/A	N/A

TABLE "D"
FINAL EFFLUENT STREAM
QUEBEC

MINE	FLOW IPGM	CNT	SCN	CNF/CNT	SCN/CNT
QA	N/A	13	64.0	0.508	4.923
QB	139	N/A	N/A	N/A	N/A
QC	208	3.3	0.5	0.970	0.152
QD	2080	3.4	8.0	0.819	2.353
QE	7-30	0.2	2.0	0.069	10.000

REFER TO TABLES A5-A8 OF APPENDIX A FOR DETAILED ANALYSES OF THESE WASTEWATER STREAMS.

mines. These ratios reflect the biodegradability of the process effluents. Since complexed cyanides, such as those of iron and cobalt, are not biologically degraded at a high level of efficiency, a large fraction of free cyanides is desirable in the effluent stream to be treated.

The SCN^-/CN^- ratio may also be an important factor since thiocyanate is more biodegradable than cyanide. Thus, a large SCN^-/CN^- ratio is probable desirable. Literature dealing with this subject has not been published yet. The critical ratios of the gold mill effluents, presented in Tables 4.2A-D, are widely variable. Thus, the biodegradability of these effluents will be very site dependent.

4.2 Silver Mill Effluents

Characteristics of a cyanide bearing effluent from a silver mill are given in Table 4.3. The biodegradability of this effluent is similar to an effluent from a gold mill.

4.3 Effluents from the Flotation of Base Metal Sulfides

As discussed in section 3.3, the principal cyanide-bearing wastewater stream from froth flotation processing is the final tailings slurry. The aqueous phase of the slurry may contain free cyanide and complex metal-cyanide compounds and other chemicals, such as reaction products of sulfur and cyanide and mineral dissolution products. The solid phase of the slurry may contain physically and chemically sorbed cyanide compounds. Most of the cyanides present in flotation tailings are in the form of complex metallocyanides, with

TABLE 4.3

CHARACTERISTICS OF SELECTED INDUSTRIAL EFFLUENT LIQUORS

Type of Effluent	pH	CN_T	SCN^-	CNO^-	NH_3	Zn	Cd	Ni	Cu	Fe
Silver Mill	11.6	56	31	5	4	36.3	0	0	11.6	0
Flotation Liquors										
Pyrrhotite Flotation	9.5	116	117	-	-	0	0	47	36	0
Copper Flotation	9.6	69	30	-	-	<0.2	0	<0.2	37	<0.02
Copper-Zinc Flotation	7.1	80	42	-	-	19	0	<0.2	41	<0.02
Tailings Slurries from Flotation Circuits (62% solids in pulp)										
Pyrrhotite	8	113	350	-	-	-	-	33	17	13
	8	152	452	-	-	-	-	30	12	11

Taken from Devuyst et al. (1982).

varying degrees of persistence in the environment, depending on whether they remain in a solid or aqueous phase (Huiatt, 1984). In the solid phase, most complexes remain inert. However, one complexed iron species (ferric ferricyanide) degrades in the solid phase and releases CO_2, N_2, and traces of other compounds. Complexes associated with flotation tailings are usually tightly bound thermodynamically stable compounds, such as metal hexacyanoferrates (eg. Cu-$Fe(CN)_6$), which do not dissociate readily (Walker and Watkins, 1968). Most investigators (Pettet and Mills, 1954; Winter, 1962) have found that effluents, containing predominantly stable complexed cyanides, are not amenable to biological degradation at a high level of efficiency.

Chemical analyses of cyanide bearing effluents from selected base metal sulfide mines are given in Table 4.3 (Devuyst et al., 1982). AMAX OF CANADA LTD. (1980) and AMAX ENVIRONMENTAL SERVICES INC. (1980) also reviewed information pertaining to the concentration of complex cyanides in flotation tailings. A summary of their findings is given in Table 4.4. Hans von Michaelis (1984) remarked that these estimates are likely to be high since some cyanides are converted in the flotation circuit by oxidation to cyanates or thiocyanates and may not report to the tailings.

4.4 Iron and Steel Industry Wastewaters

Characteristics of coke plant wastewater (raw weak ammonia liquor) are given in Table 4.5a. Raw weak ammonia liquor (WAL) contains relatively high concentrations of phenols, thiocyanate, cyanide and ammonia. If the concentrations of cyanide and ammonia are first reduced by distillation, this wastewater can be biologically

TABLE 4.4

ESTIMATED MAXIMUM PROBABLE
CONCENTRATION OF CYANIDE IN BASE METAL SULFIDE FLOTATION TAILINGS

Plant No.	Mine Type	Cyanide Added lb/ton	Ore Processed tons/day	Probable Concentration of Cyanide in Tailings ppm
A	Cu/Mo	0	60,000	0
B	Cu/Mo/Ag	0	92,000	0
C	Cu	0	50,000	0
D	Cu	0	42,000	0
E[2]				
F[2]	Cu/Mo/Others	0.02	105,000	5
G[2]				
H[4]	Lead/Zinc/Cu	0.05	5,000	10
I[4]	Lead/Zinc/Cu	0.05	7,500	10
J[4]	Lead/Zinc/Cu	0.05	5,000	10
K[4]	Lead/Zinc/Cu	0.05	2,500	10
L	Lead/Zinc/Cu	0.02	4,200	1
M	Lead/Zinc	0.01	6,500	5
N	Zinc/Copper	0.1	7,000	35
O[3]	Zinc	0.0-0.02	6,500	5
P[3]	Zinc	0.0-0.02	3,200	5
Q[3]	Zinc	0.0-0.02	1,900	10

1. Data from US EPA Contract No. 68-03-2552.
2. Plants E, F and G reported as one facility
3. Intermittent usage; estimated using ore feed as tailings estimate since ore: Tailings ratio is approximately 1:1.
4. Suppress zinc and iron; zinc recovered due to intermittent iron suppression.

Source: AMAX ESI (1980)

treated. Characteristics of a pretreated weak ammonia liquor, which has been used as feed to a single-stage activated sludge process, are also given in Table 4.5a.

One approach, used in the pilot plant investigations at the Wastewater Technology Centre in Burlington, Ontario (Nutt et al., 1982b), is to combine pretreated coke plant wastewater with blast furnace blowdown wastewater. Biological treatment of blast furnace blowdown water, alone, is not commonly practised since the low concentration of organic contaminants is inadequate to support biological growth. The characteristics of the separate and combined wastewater streams are given in Table 4.5b.

4.5 Cyanide Bearing Effluents from Aluminum Production

Characteristics of the leachate from the spent potlining piles are given in Table 4.6. These waste streams are difficult to characterize because wastes from other parts of the aluminum processing plant, as well as occasional spills from wet scrubbers, and the Bayer process are also incorporated (Alcan Research Centre, private communication). The actual volumes of wastewater can vary by an order of magnitude. Consequently, the concentration of the various compounds fluctuate enormously. For example, the pH of these streams can vary from 3 to 12 for short periods of time. A reasonable average value is approximately 9.5. Fluoride concentrations might go as high as 1 g/L but are more normally below 20 ppm. Suspended solids at the entry to the pond might be as high as 1.0 % but are more normally about 0.1 %. The concentration of total cyanide in the various streams is normally in the 0.05 ppm range and rarely exceeds 5 ppm.

TABLE 4.5A

CHARACTERISTICS OF RAW WEAK AMMONIA LIQUOR AND PRETREATED WAL

Parameter	Concentration (mg/L)*	
	Raw WAL**	Pretreated WAL***
pH	8.5	N/A
COD	5,000 - 10,000	N/A
Phenol	1,000 - 2,800	200
CN_T	20-80	1 - 2
NH_3	4,000 - 5,000	50 - 100
SCN^-	700 - 1,300	250
Thiosulfates	1,000	N/A
Cl^-	10,000	N/A

* except pH
** Cousins and Mindler, 1972
*** Gauthier et al., 1981

TABLE 4.5B

CHARACTERISTICS OF COKE PLANT AND BLAST FURNACE BLOWDOWN WASTEWATERS AND THE COMBINED WASTEWATER

PARAMETER ($mg \cdot L^{-1}$)	COKE PLANT WASTEWATER	BLAST FURNACE BLOWDOWN		COMBINED WASTEWATER
		SYSTEM A	SYSTEM B	
FOC	550.	11.	8.	215.
Phenolics	241.	5.1	0.1	119.
NH_3-N	183.	22.1	33.4	66.4
CNS	290.	3.3	1.7	98.1
TCN	5.0	5.3	1.6	1.8
CN_A	2.4	5.2	1.5	0.5
TKN	307.	28.2	40.0	111.
Total Zinc	0.4	20.3	6.1	2.0

(Taken from Nutt et al., 1982b)

The cyanides are largely complexed as ferrocyanides by the time they reach the ponds, with perhaps only 10 % free cyanide.

TABLE 4.6

CHARACTERISTICS OF LEACH LIQUORS FROM SPENT POTLININGS

Stream Designation	Characteristics
Stream A 15 MGD leach liquor circulated through ore plant	CN^- 0.05-5 mg/L pH 2-12 F^- 20-1000 mg/L Suspended Solids 0.1-1 %
Stream B 0.2-20 MGD leach liquor	0-1 ppm CN (concentration depends upon rainfall) approximately 1/3 is free cyanide and 2/3 is complexed as ferrocyanide pH 9.0-9.5 (fairly stable) 2-3 ppm Fe

Courtesy of Alcan Research Centre, Kingston, Ont.

Due to the large variations in flow rates and concentrations, and the presence of the very stable ferrocyanide complex, a biological reactor may not be a viable alternative for treatment of these wastewaters.

5.0 TOXICITIES OF CYANIDE BEARING EFFLUENTS AND EFFLUENT REGULATIONS

5.1 Toxicities of Free and Complexed Cyanides to Aquatic Species

Fish toxicity data for hydrogen cyanide and various metal cyanide complexes are summarized in Table 5.1. Free cyanide toxicity to man, mammals and aquatic species is well documented (Doudoroff, 1976, Ecological Analysts, 1979, Towill et al., 1978). Undissociated HCN is more toxic towards aquatic life than CN^- alone; HCN remains largely undissociated at pH values of 8 or less. Generally, free cyanide concentrations greater than 0.1 mg/L are expected to kill sensitive species in freshwater or marine environments (Doudoroff, 1976). Several variables can affect the degree of free cyanide toxicity: pH, water exchange, temperature, oxygen content of water, ionic strength, species acclimation and body size. A summary of these variables was reported by Huiatt et al. (1983).

Complexed cyanides are reported to be less toxic than free cyanides. However, complexed cyanides undergo varying degrees of dissociation when in solution and release free cyanide (Caruso, 1975). The degree of toxicity of solutions of complexed cyanides is dependent upon the amount of free cyanide present (Doudoroff, 1976; Smith et al., 1979). Certain complexes that are readily dissociated in aqueous solution (zinc cyanide, cadmium cyanide) are highly toxic because of the availability of free cyanide. On the other hand, metals which form moderate to strong complexes, such as nickel, may complex with cyanide to reduce lethality, expecially at higher pH values. Doudoroff et al. (1966), by comparing the median survival time (MST), and the free cyanide levels in simple cyanide solutions (NaCN) and in

TABLE 5.1

SUMMARY OF FISH TOXICITY DATA FOR CYANIDE COMPOUNDS

Cyanide Species	Comments
HCN and CN^-	more toxic in undissociated form (ie. below pH 8)
Zn Cyanides	Slightly more toxic than the equivalent amount of HCN
Cd Cyanides	Slightly more toxic than equivalent amount of HCN
Ag cyanides	Median lethal range is 6-10 mg/L CN_T. Rate of tissue penetration by the silver cyanide ion is slower than Cu. Thus, the toxicity is less than expected. However, silver is not a big problem in most wastes.
Ni Cyanides	Forms stable cyanide complex. Present in slightly alkaline waters at concentrations greater than 100 ppm without harm to fish life. Non-toxic if pH > 7.5 for 500 mg/L CN_T. However, the complex breaks down and releases HCN in acid waters, thereby increasing toxicity.
Cu Cyanides	Evidence that Cu reduces the toxicity of cyanide. At pH 7, the predominant species are $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$. At alkaline conditions, less toxic than HCN. More toxic as pH is dropped due to dissociation to form free cyanide. Toxic level is approximately 4 mg/L CN_T.
Fe(II) cyanide	Toxicity, in the absence of light, is due to the equilibrium concentration of HCN. In the presence of sunlight, concentrations as low as 1 mg/L are toxic.
Fe(III) cyanide	Ferric cyanide is less stable than ferrocyanide and therefore is the more toxic of the two.

Complexes are listed in order of increasing stabililty. It has been suggested that the toxicities of the metal cyanide complexes are inversely related to their stabilities. Although this trend is generally true, exceptions arise since kinetic factors are also involved. Silver cyanide, for example, is less toxic than expected because the rate of tissue penetration is slow.

(Data adapted from Ingles, 1981)

complex cyanide solutions, identified the active component(s) responsible for mortality of bluegill fish. The toxicity of metallocyanide complexes was attributable almost solely to the concentration of free cyanide in equilibrium with the complex. The concentration of free cyanide depends markedly on pH because pH strongly influences the dissociation of the metallocyanide complex.

Lordi (1980) reported the toxicities of cyanide bearing wastewaters discharged to sewers in Metropolitan Chicago. The range of total cyanide levels in the studied effluents was from 0.004 to 0.15 mg/L. The results of bioassay tests, using fathead minnows, showed that there was no correlation between total cyanide concentration and the percent survival of the fathead minnow. However, the cyanides occuring in the effluents were primarily complex cyanides, which had a significantly lower toxicity than free cyanide. In general, 100% survival occurred with total cyanides up to 0.15 mg/L.

Conflicting opinion, regarding the hazards associated with the iron-cyanide complexes, exists because of their tendency to undergo photodecomposition in the presence of ultraviolet radiation, with the subsequent release of free cyanide. Although the photodissociation of iron cyanides in the laboratory to free cyanide gives toxic effluents to aquatic life at about 1.0 mg/L (Lordi, 1980), it is difficult and misleading to extrapolate these findings to the natural environment because of the influence of many factors, such as pH, temperature, sunlight, turbidity, phytoplankton, and the presence of other compounds. Photodecomposition of iron cyanide complexes is

time-dependent and may be negligible in deep, turbid, or shaded waters. This position is corroborated by Doudoroff (1976).

5.2 Toxicity of Thiocyanate to Aquatic Species

Compared to cyanide, thiocyanate is relatively harmless; however, it should not be treated as an innocuous compound. The median toxicity of thiocyanate is of the order of 90-200 mg/L CNS^- (Ingles, 1981). The unusual aspects of thiocyanate's toxicity to fish are:

i) Its action is much slower than that of cyanide; while fish can tolerate quite high concentrations for 24 hours, much lower levels are lethal over a longer period (144 h).

ii) The physiological changes it induces appear to be irreversible, since death of the test specimens ensues at about the same time interval even if the fish is returned to clean water after a relatively short exposure to the thiocyanate solution.

The toxicity data of thiocyanate to aquatic animals have been recently published by Meyer and Hemming (1983).

5.3 Toxicities of Gold Mill Final Effluents Relative to the Environmental Regulations

The Ontario objectives for mineral processing effluents are given in Table 5.2A. Cyanides are regulated at two points. Cyanides should be reduced to less than 2 mg/L. This is an interim guideline. As the availability of practicable technology permits, cyanide dicharges should be reduced to the lowest levels attainable. Cyanide

TABLE 5.2A

ONTARIO EFFLUENT OBJECTIVES FOR THE MINERAL PROCESSING INDUSTRY

Item	Effluent Guideline
pH	5.5-10.6 (sudden changes to be avoided)
BOD_5	< 15 mg/L
Suspended Solids	< 15 mg/L
Oil & Grease	< 15 mg/L
NH_3**	< 10 mg/L
Total of Cu,Pb,Zn,Ni,	< 1 mg/L
Cd, Hg	Not to exceed background concentrations
Other metals	< 1 mg/L per metal (except Ca, Mg, K, Na)
Total P	< 1 mg/L
As	< 0.5 mg/L
Phenols	< 20 ppb
CN_T	< 2 mg/L (expressed as HCN)
SO_4	lowest possible, best available technolgy
Total Dissolved Solids	lowest possible, best available technolgy
Colour	clear and colourless
Unstable species	Not to exceed levels which cause adverse environmental effects

** At control point

Source : MOE Document "Guidelines for the Environmental Control in the Ontario Mineral Industry" October 1, 1981.

TABLE 5.2B

CYANIDE EFFLUENT REGULATIONS IN VARIOUS PROVINCES AND TERRITORIES

Location	CN^- Concentration limit
British Columbia	0.05 mg/L
North West Territories	0.05 mg/L
Quebec	variable

effluent regulations for other provinces in Canada are listed in Table 5.2B.

Toxicity data for final effluents released by a few Canadian gold mines are given in Table 5.3 (Scott, 1984a). Many effluents do not meet the recommended effluent guidelines and are also highly toxic. Thus, a need exits for a treatment process to remove cyanide and heavy metals (primarily copper and zinc) from these wastewaters.

TABLE 5.3

TOXICITIES OF GOLD MILL FINAL EFFLUENTS

Final Effluent									
As	Cu	Pb	Zn	SS	pH	CN_T	CN_w	Year	Toxicity
.005	0.12	0.07	40	50	5.0	0.14	0.01	1982	LT50 < 15h*
.004	0.1	.012	.02	20	8.9	.01	.01	1982	NA
.001	0.1	0.1	0.06	3000	7.9	0.87	0.42	1982	LT50 > 96 h
.012	0.32	0.02	2.54	36	10.5	21	16.2	1982	LT50 < 10 min.
0.01	16.5	0.04	15.6	17	9.5	61	42	1982	LT50 < 5 min.
.001	3.65	-	3.04	56	74	3.3	3.1	1982	LT50 = 24 h
-	1.35	0.02	.05	20.0	7.3	2.8	0.34	1982	LT50 < 0.5 h
.002	8.15	.02	2.64	10.0	8.8	25	18.6	1982	LT50 < 15 min.
.002	1.00	.04	1.32	13.0	7.4	4.8	4.5	1982	LT50 < 10 min.
1.8	.03	-	.005	35	8.3	0.12	.02	1982	LT50 > 96 h
.002	7.0	-	-	NA	7.6	8.75	NA	1981	96hLC50 = 24%
0.30	0.86	-	0.02	15	8.6	4.4	NA	1981	96hLC50 = 29%

LT50 - Time which 50% of the test organisms are dead in a given effluent (96 h or less)
LC50 - Portion of an effluent (in %) that kills 50% of the test species in 96 h
SOURCE : J.S. Scott (1984)

6.0 CURRENT METHODS OF CYANIDE REMOVAL

A review of treatment methods, available for the removal of cyanide from wastewaters, may be found in a paper by Ingles and Scott (1981). Until recently, the treatment of waste waters from gold mills was limited to natural degradation in tailings ponds (Scott, 1984a) where the major mechanism for the removal of cyanide is volatilization of HCN. One exception to the sole use of natural degradation was the very limited application of the acidification-volatilization process. Over the past 4-5 years a number of gold mining companies have applied chemical treatment for the removal of cyanides. A summary of the effluents treated and the treatment methods used is given in Table 6.1. As discussed in Section 10, chemical costs are exceptionally high and cyanide concentrations are not usually reduced to nontoxic levels (Mudder and Whitlock, 1984).

To assess the applicability of biological treatment for cyanide bearing effluents from Canadian mineral processing industries, the cyanide degrading organisms need to be identified and available biological processes need to be evaluated. In addition, the limitations of a biological treatment process need to be determined. Each of these topics are addressed in the remainder of the report.

TABLE 6.1

SUMMARY OF MINES USING CHEMICAL TREATMENT METHODS

Company	Gold Refining Process	Effluent Treated	Treatment Method
Giant Yellowknife N.W.T.	CIP	tailings pond	alkaline chlorination overflow
Detour Lake Ont.	CIP	slurry from mill	alkaline chlorination
Mosquito Creek B.C.	Merril-Crowe	barren bleed	alkaline chorination*
Baker	Merril-Crowe	barren bleed	alkaline chlorination (batch wise treatment using calcium hypocholorite)
Scottie B.C.	Merril-Crowe	1) barren bleed 2) mill tails(55% solids)	Inco SO_2 process
McBean	Merril-Crowe	barren bleed	Inco SO_2 process
Equity**	CIP	slurry	Inco SO_2 process

* Currently investigating pilot plant using tailings pond overflow since treatment of barren bleed has not been very successful

** Primarily a silver mine with a gold scavenger process.

Source: J.S. Scott, private communication

7.0 CYANIDE ASSIMILATION BY CYANOGENIC MICROORGANISMS

This section is organized into five parts. The objectives of the first three subsections (7.1 - 7.3) are to identify the groups of microorganisms that may be useful in the treatment of cyanide bearing effluents and to summarize the reported metabolic pathways by which cyanide assimilation occurs. The degradation of thiocyanate is considered in the fourth subsection since many cyanide bearing wastewaters contain this species also. To complete the discussion, the selective use of microorganisms is examined.

7.1 Organisms Capable of Cyanide Degradation

Few organisms are tolerant of hydrogen cyanide. Cyanide irreversibly binds with the iron group of cytochrome oxidase, an enzyme concerned with cellular oxidation, thereby, making the cytochrome oxidase inactive. Death ensues because utilization of oxygen for an important metabolic reaction is prevented. In tolerant organisms, the bases for resistance to cyanide have varied from formation of a cyanide resistant cytochrome oxidase (Arima and Oka, 1965; Oka and Arima, 1965) to cyanide utilization (Skowronski and Strobel, 1969).

The species or groups of organisms that have been reported to assimilate cyanide are listed in Table 7.1.1. In general, these organisms are indigenous to soil. Many of these bacteria are also capable of reproduction via spore formation. This is significant, since spores possess properties which enable them to resist the destructive effects of physical and chemical agents. Most

TABLE 7.1.1

ORGANISMS REPORTED TO ASSIMILATE CYANIDE

Organism	Reference
Fungi	
Fusarium moniliforme	Powell et al. (1983)
Fusarium solani	Shimizu et al. (1969) Mimura et al. (1972)
Gloecercospora sorghi	Powell et al. (1983)
Mycoleptodiscus terrestris	Powell et al. (1983)
Marasmius oreades	Allen and Strobel (1966)
Pholiota adiposa	Allen and Strobel (1966)
Pholiota aurivella	"
Pholiota praecox	"
Rhizopus nigricans	"
Psychrophilic basidiomycetes	Strobel (1964,1967)
Stemphtlium loti	Fry and Millar(1972)
Bacteria	
Arthrobacter	Aaslestad, in Murphy (1964)
Alcaligenes viscolactis	Fujii and Oshimi (1973)
Achromobacter nitriloclastes	Fujii and Oshimi (1973)
Actinomyces	Ware and Painter (1955) Pettet and Ware (1955) Gurnham (1955) Brunker (1980)
Nocardia	Winter (1962) Kato et al. (1976)
Bacillus pumilus (Fargo clay)	Skowronski and Strobel (1969)
Bacillus megaterium (Fargo clay)	Castric and Strobel(1969) Raef et al. (1977b)
Bacillus stearothermophilus	Atkinson (1975)
Chromobacterium violaceum	Brysk et al.(1969) Rodgers and Knowles (1978)
Escherichia coli	Dunnill and Fowden (1965)
Pseudomonas nonliquefaciens	Putilina (1961)
Pseudomonas paucimobilis	Mudder and Whitlock (1984c)

sporeforming genera are to be found among the Actinomycetes. However, Bacillus is characterized in part by its ability to produce spores.

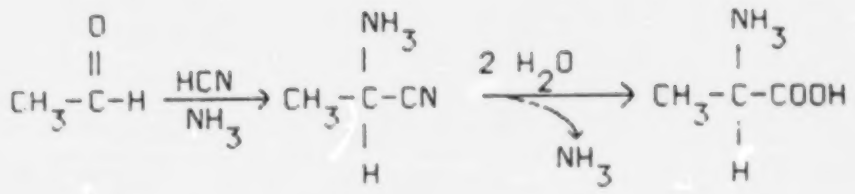
The metabolic pathways for cyanide conversion in these fungi and bacteria are discussed in the next two sections. Some investigators report that a supplemental carbon source is unnecessary since cyanide is used both as a carbon and nitrogen source. Other investigators report that cyanide is used as a nitrogen source only. An understanding of the details of the metabolic pathways is essential for the interpretation of these contradictory views. (To omit these details, the reader is refered to Section 7.4.)

7.2 Metabolic Pathways of Cyanide Conversion in Fungi

Strobel (1964) first showed that a psychrophilic basidiomycete could assimilate cyanide. Mycelia incubated with $H^{14}CN$ for 20 h at 13°C, were harvested, disrupted, and the cells fractionated. The only labeled amino acids were alanine and, to a lesser extent, glutamate. In shorter-term experiments, alanine was the only labeled amino acid. Control studies with $^{14}CO_2$ illustrated that cyanide was not converted to CO_2 before assimilation.

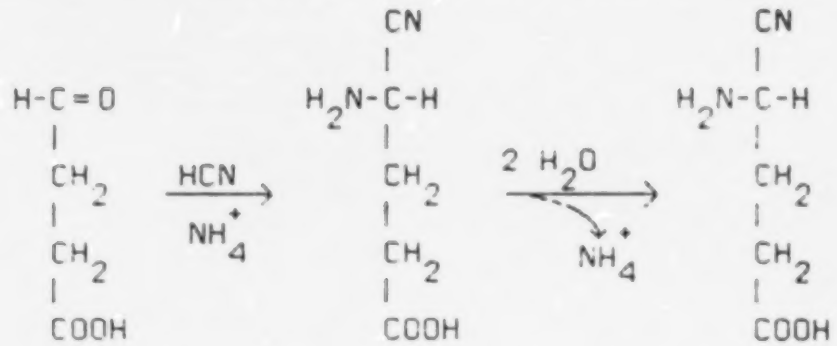
A metabolic pathway for the formation of L-alanine in the psychrophilic basidiomycete was proposed in a subsequent study by Strobel (1966). The label in $H^{14}CN$ appeared in α-aminopropionitrile during the first 12 h of incubation and then decreased, whereas, the quantity of radioactive alanine increased steadily for 24 h. When $H^{14}C^{15}N$ was used as the substrate, carbon labeling appeared exclusively in the C1 position of both products and nitrogen labeling appeared in the cyano group of α-aminopropionitrile. Strobel

suggested that the results are consistent with the following pathway:



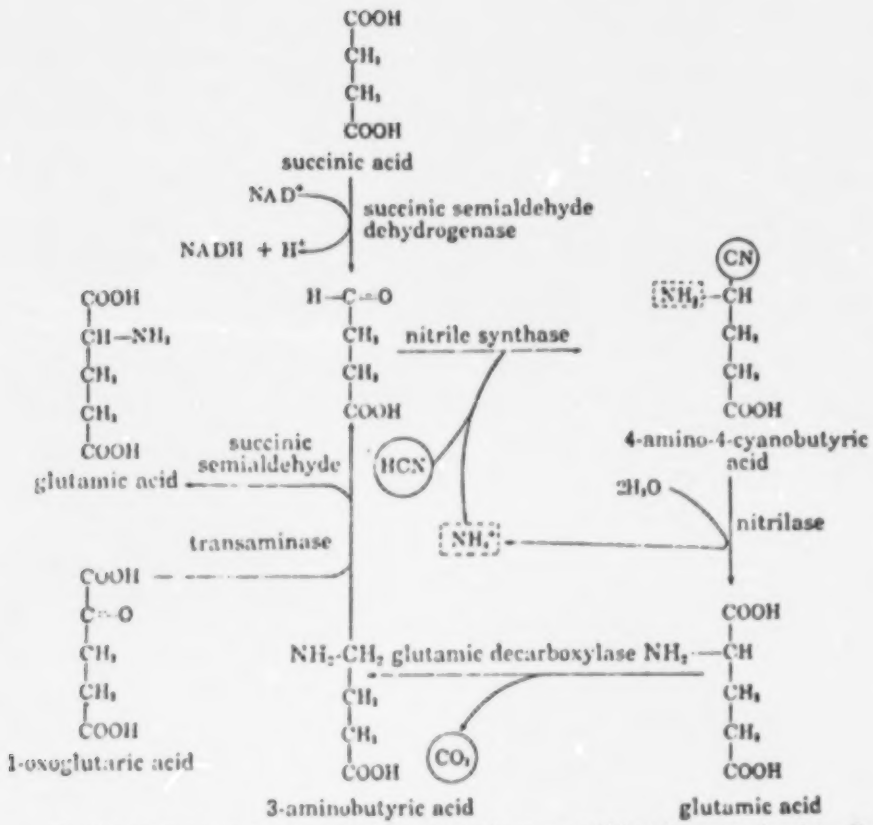
acetaldehyde α-aminopropionitrile L-alanine

A metabolic pathway for glutamate formation was established in another study by Strobel(1967b). Glutamate is derived from cyanide and succinic semialdehyde via 4-amino-4-cyanobutyric acid:



Proposed scheme of glutamate formation from cyanide via 4-amino-4-cyanobutyric acid in a psychrophilic basidiomycete

Cyclic conversion of cyanide to CO_2 was proposed by Strobel, based on experimental data from these studies. The pathway, illustrated below, would serve to detoxify the cyanide, possibly by the assimilation of the cyanide-nitrogen, but there would be no assimilation of cyanide-carbon by the organism.



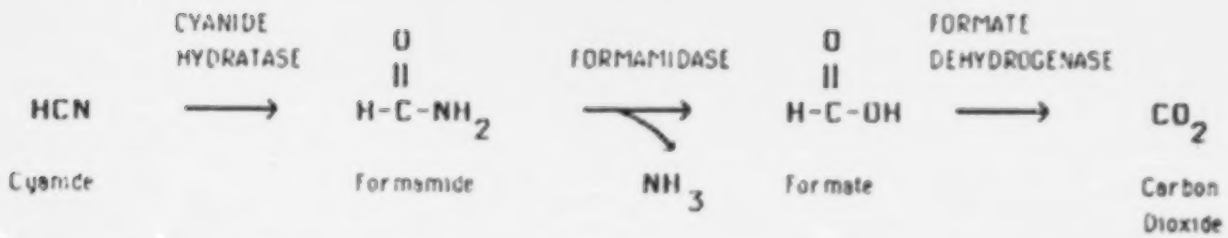
Possible pathway for detoxication of cyanide by the snow mold basidiomycete, involving formation of 4-amino-4-cyanobutyric acid.

(Knowles, 1976)

Allen and Strobel (1966) tested cyanide assimilation by several other fungi. Marasmius oreades, Pholiota adiposa, Pholiota aurivella, Pholiota praecox, and Rhizopus nigricans incorporated $H^{14}CN$ into alanine and to a lesser extent other amino acids, whereas Fusarium nivale incorporated cyanide into asparagine only. Pholiota aurivella appeared to be most capable of fixing HCN. Cyanide was metabolized to NH_3 and an unidentified compound by Fusarium solani (Shimizu, et al. 1969).

Fry and Millar (1972) isolated an enzyme, formamide hydrolyase, from the fungus Stemphyulium loti which converts cyanide to formamide. Cyanide tolerance of Stemphyulium loti differs from that exhibited by many other organisms in that it is induced upon exposure of S. loti to cyanide (adaptation), and protein sythesis is a requirement for adaptation. Cyanide tolerance of S. loti apparently depends on its capacity to convert cyanide into other compounds.

In a subsequent study by Powell et al.(1983), several fungi were evaluated for their ability to degrade cyanide. Of these, three organisms were determined to be outstanding in their ability to degrade cyanide: Fusarium moniliforme, Helminthosporium sorghicola, and Mycoleptodiscus terrestris (See Table 7.1.2). The pathway of cyanide detoxification in Fusarium moniliforme is given below:



The pathway of Cyanide detoxification in *Fusarium moniliforme*

TABLE 7.1.2

ACTIVITIES OF CYANIDE HYDRATASE IN CYANIDE DETOXIFYING FUNGI

Fungi	µmoles cyanide degraded/ min/mg protein
Gloecercospora sorghi*	19.6
Fusarium moniliforme	16.1
Mycoleptodiscus terrestris	15.6
Helminthosporium sorghicola	14.5
Stemphylium loti	5.2
Cochliobolus victoriae 6327	4.2
Cochliobolus victoriae 2000	3.1
Glomerella tucumanensis	1.6

* This value was reported as 19.6 by Nazly et al.(1983) and as 7.0 by Powell et al. (1983). The reported value of 7.0 was judged to be an error in the text.

Beardsmore et al. (1982) developed batch and continuous reactor treatment systems, utilizing the cyanide hydratase enzyme which is extracted from these fungi. However, since the fungi are not alive, cyanide is converted to the intermediate product, formamide. Further discussion of this treatment process is given in Section 8.7.

In conclusion, the metabolic by-products of fungi are ammonia and carbon dioxide. Cyanide does not appear to be used as a carbon source for growth for the fungi reported in this section. Therefore, a supplemental source of carbon is necessary. Metabolic pathways for cyanide conversion in bacteria are presented in the next subsection.

7.3 Metabolic Pathways for Cyanide Conversion in Bacteria

Ware and Painter (1955) isolated a bacterium, in the family Actinomycetaceae, capable of utilizing up to 150 mg/L of cyanide. It is slow growing, aerobic, and a strict autotroph. Growth is best at cyanide concentrations of 40 mg/L. It uses KCN as a source of nitrogen and carbon. Ammonia is produced quantitatively by the growth of the organism but the fate of the carbon was not known. Further work by Pettet and Ware (1955) provisionally placed the organism in the genus: Actinomyces. It grows on silica gel as hard powdery pure white colonies. The optimum temperature for growth is below 30°C; the organism is not resistant to drying. Growth of the organism is enhanced by traces of iron, magnesium and copper. Good growth occurs only between pH 7.5 and 9.0. It is unable to grow on glucose-ammonium salts or peptone media.

Winter (1962) characterised two aerobic cultures capable of degrading 45-105 ppm levels of KCN at 90 per cent efficiency or greater. The cultures were placed in the family Actinomycetaceae, genus: Nocardia. The cultures utilize paraffin and glycerol but not phenol. Growth is optimum between 25-30°C. These cultures differ from the Actinomyces in the following characteristics:

i) they were not innibited by organic materials

ii) growth was rapid and quite profuse

iii) the organisms were characteristically made up of smooth filaments rather than knobbly filaments

iv) they were capable of greater reduction of cyanide compared to Actinomyces

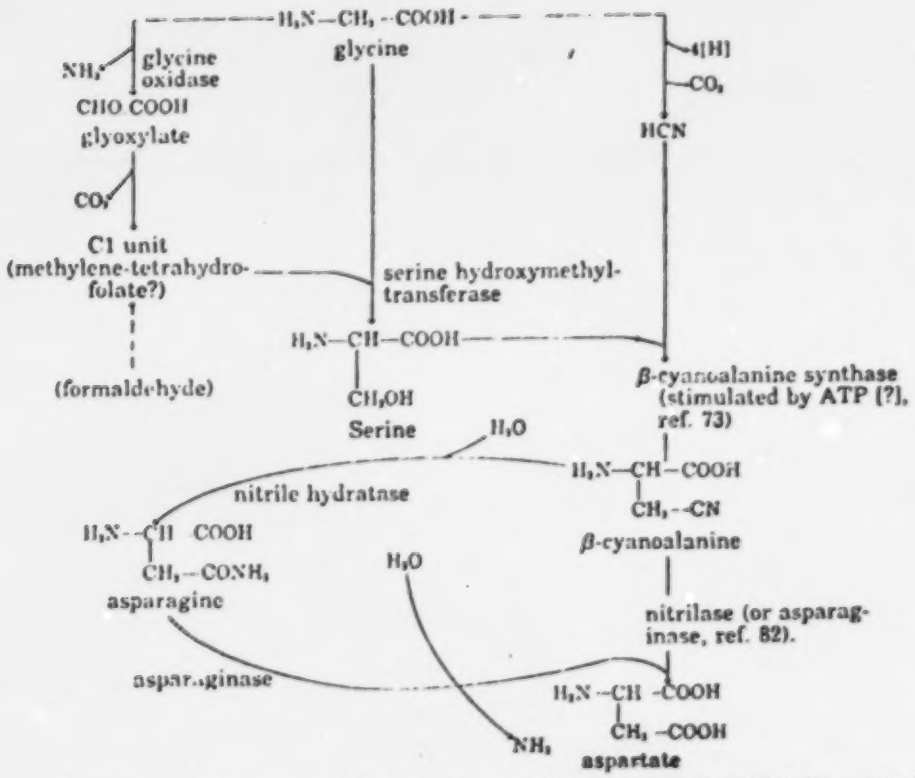
A process utilizing these organisms for cyanide degradation was reported by Kato et al. (1976).

Skowronski and Strobel(1968) isolated a filamentous strain of Bacillus pumilus, which is capable of utilizing cyanide and can survive in KCN concentrations up to 2.5 M. The bacterium was isolated from Fargo clay in a field near Fargo, North Dakota which had been cropped in flax for 73 years. The optimum conditions for growth of the new strain, in a medium containing 0.1 M KCN, were: pH 8.5-9.0, temperature of 40°C and an agitation rate of 50 r.p.m. Under these conditions the generation time was 44 minutes. Filaments may be induced by a variety of environmental conditions, such as the presence of poisons and metabolic inhibitors, nutritional deficiencies, and other physical conditions. However, in contrast to other bacteria that form filaments, the filamentous type of Bacillus pumilus does not revert to the normal bacilliform when cultured on mediums not containing KCN.

Cyanide utilization by the Fargo clay strain of Bacillus pumilus was confirmed by labelling studies using $K^{14}C^{15}N$. The formation of $^{14}CO_2$ and $^{15}NH_3$ suggests that the cyanide carbon and nitrogen make their way through a common metabolic intermediate. It was suggested that the bacterium uses endogenous substrates and

thereafter cyanide as the principal carbon source. Detectable quantities of cyanide were not found in the bacterium.

Studies by Brysk, Corpe, and Hankes (1969) show that Chromobacterium violaceum forms β -cyanoalanine and aspartic acid from cyanide. The 3-carbon precursor was postulated to be serine. In addition, α-cyano-γ-aminobutyric acid is formed although no further metabolism appears to occur, suggesting that it is a detoxification product (Brysk and Ressler, 1970). C. violaceum also forms rhodanese as a possible detoxifying agent (Rodgers and Knowles, 1978).



Incorporation of cyanide and glycine into β-cyanoalanine and asparagine by C. violaceum strain 9.

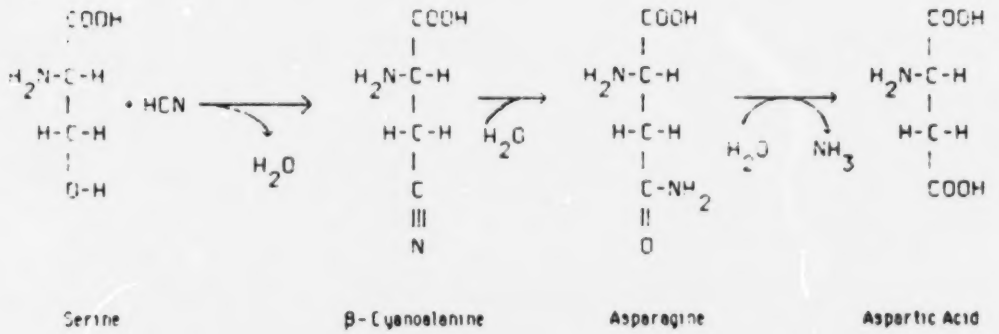
(Knowles, 1976)

The enzyme rhodanese, which catalyzes the formation of thiocyanate and sulfite from cyanide and thiosulfate has been found in various organisms including Escherichia coli and Bacillus subtilis (Villarejo and Westley, 1963; Bowen et al., 1965). Thiobacillus denitrificans has the highest levels of this enzyme (Bowen et al., 1965). B. stearothermophilus has been reported to produce equally high rhodanese levels (Atkinson et al.,1975). The use of this organism in a small chemical reactor for the continuous conversion of cyanide to thiocyanate was subsequently reported by Atkinson (1975).

Dunnill and Fowden (1965) have obtained an enzyme preparation from E. coli which forms β -cyanoalanine from cyanide and serine. The specificity of the 3-carbon precursor to β -cyanoalanine is uncertain since serine appeared to serve as a substrate, however, a competitive effect is noted with cysteine.

Castric and Strobel (1969) isolated a cyanide metabolizing strain of Bacillus megaterium from Fargo clay. The organism was grown on Trypticase soy broth containing 65 mg/L (1 mM) cyanide; growth coincided with cyanide disappearance from the medium. When $K^{14}CN$ was added to the medium, the label was incorporated into CO_2, the amide carbon of asparagine, and the C4 carboxyl of aspartate. Washed cells fed serine converted it to β -cyanoalanine and asparagine, and cells fed β -cyanoalanine converted it to asparagine, but β -cyanoalanine was not detected during conversion of serine to asparagine by cell-free extracts: possibly nitrilase activity for conversion to β -cyanoalanine to asparagine is more active than β -cyanoalanine synthase activity under the conditions used in the latter experiment. Cysteine did not act as a substrate for β -cyanoalanine or asparagine

synthesis in extracts or in washed cell suspensions. It was proposed that β -cyanoalanine was synthesized from serine and cyanide, which was converted to asparagine and then aspartate.



A pathway of aspartic acid biosynthesis in *B megaterium*

Furuki et al. (1972) isolated a strain of bacteria which utilized cyanide as a nitrogen source. The bacteria was isolated from soil which had been polluted with waste water from an electroplating plant. The bacterium grew well in in mediums containing 400-500 ppm cyanide, but growth was gradually inhibited with increasing cyanide concentration. The bacterium also utilized urea, ammoniacal nitrogen, and peptone, while it could not utilize nitrous, nitrate or nitrile nitrogens. Glucose, fructose, mannose, and galactose were utilized as carbon sources. The bacterium showed several peaks of activity for cyanide degradation at pH 5.3, 7.0, and at 10.0. At pH 10.0, degradation activity was the highest in the cells of the exponential growth phase, and lower in the subsequent growth phase.

Putilina (1961) reported the isolation of a thiocyanate user, Pseudomonas nonliquefaciens, which can also use cyanide as a carbon and nitrogen source.

Manzoku et al. (1979) reported the treatment of a wastewater containing 500 mg/L cyanide with a mixture of microorganisms selected from the group: Asperigillus restrictus, A. versicolor, Cladosporium cladosporiodes, Paecilomyces varioti, Penicillium charlesii, P. citrinum, and P. implicatum. The concentration was reduced to 1 mg/L by biologically digesting the cyanide solution with P. implicatum at pH 7 for 1 h.

Mudder and Whitlock (1984c) have patented a bacterium, Pseudomonas paucimobilis mudlock, for the degradation of cyanides and thiocyanates. Dissolved organic matter in the wastewater provides the nutrient for growth for the microorganisms used in the Homestake process.

In conclusion, most of the identified bacteria are aerobic and heterotrophic. Cyanide is used as a nitrogen source. A few of the identified bacteria also use cyanide as a source of carbon. Carbon dioxide and ammonia are the degradation products. Optimum growth conditions are: approximately 40 mg/L cyanide, pH 7.5-9.0, and temperatures less than 35°C.

The biological decomposition of thiocyanate is considered in the next subsection.

7.4 Biological Decomposition of Thiocyanate

Substantial concentrations of thiocyanates are present in coke plant effluents (from 50 to 500 mg/L) and in gold mill effluents (from 40-400 mg/L in barren bleed; from 16-120 mg/L in tailings repulp). Thus, the biological degradation of thiocyanates must also be discussed.

In 1952, Happold et al. isolated autotrophic microorganisms capable of oxidizing thiocyanate. A detailed description of one of these organisms, Thiobacillus thiocyanoxidans, was presented in a following paper by Happold et al. (1954). Further studies on the metabolism of Thiobacillus thiocyanoxidans were performed by Youatt (1954). It was concluded that thiocyanate is first hydrolysed to cyanate and sulphide. Cyanate is further hydrolysed to carbon dioxide and ammonia; sulphide is oxidized to sulphate.

Thiocyanate can also be oxidized by heterotrophic bacteria. Stafford and Callely (1968) reported the isolation of a heterotrophic bacterium, similar to Pseudomonas stutzeri, which utilizes thiocyanate as its sole source of cellular nitrogen and which also utilizes sulphur. Both phenol and thiocyanate were metabolized simultaneously. However, the presence of excess ammonium ions inhibited the utilization of thiocyanate. The latter implied that ammonium ions lay on the pathway of nitrogen assimilation from thiocyanate.

7.5 Selective Use of Microorganisms

Although simple studies using pure cultures of microorganisms and single substrates are valuable, if not essential, for determining biochemical pathways, they cannot always be used in predicting biodegradability or transformation in treatment systems (Kobayashi and Rittmann, 1982). First, substances that cannot be significantly changed in pure-culture studies, often will be degraded or transformed under mixed culture conditions. A good example of this type of interaction is cometabolism, in which a compound, the

cometabolite, is not metabolized as a source of carbon or energy, but is incidentally transformed by organisms using other similar compounds. Second, products of the initial transformation by one organism may be subsequently broken down sequentially by a series of different organisms until compounds that can be metabolized by normal metabolic pathways are formed.

Several approaches may be used to select a suitable microbial population for the degradation of a substrate. A mixed population may be gradually and slowly acclimated to the wastewater environment. For example, when complete-mix activated sludge processes were first employed to treat steel industry wastewaters, microorganisms from municipal waste treatment processes were used as the inoculum. Although this population was not initially able to remove phenol, thiocyanate and the other pollutants, microbial selection occurred over a period of several weeks, resulting in a mixed population able to withstand the physical conditions of the wastewater and able to utilize the soluble components and nutrients.

Alternatively, a mixed culture, previously adapted to the toxic component, may be used as an inoculum. Organisms from local water or soil samples, contaminated with the toxic component, may be used (Furuki et al., 1972; Mudder and Whitlock, 1984). Seed can also be obtained from biological reactors from industries producing similar wastewaters (eg. coke plant wastewater). Some companies market specialized mutant bacterial cultures, eg. PHENOBAC; each culture capable of degrading a variety of toxic substances.

An approach, used by several investigators (Fujii and Oshimi, 1973; Raef et al., 1977b; Kato and Yamamura, 1976), is to

inoculate a mixed bacterial sample from a sewage treatment plant with an organism (Alcaligenes viscolactis, Achromobacter nitrilolastes, Bacillus megaterium, or Nocardia rubropertincta) which is known to degrade the toxic component of interest. An advantage probably exists in using mutant bacterial cultures from the last two approaches, since acclimatization will occur more quickly. However, the use of mixed bacterial cultures by the above investigators, does not neccessarily imply that a pure strain of the cyanide degrading bacteria could not be used.

A practical method for assuring proliferation and maintenance of selected populations involves controlling environmental factors. Key control parameters are pH, loading rate of the toxic component, nutrient and trace element availability, moisture content, and temperature. Consideration must also be given to the needs of the interacting organisms that may be involved. This is clearly the case in the treatment of cyanide bearing wastewaters, since nitrifiers are required to convert the ammonia to nitrate and nitrite. In some cases a series of biological reactors are required to provide the different environmental conditions necessary for complete biodegradation.

The candidate biological processes for cyanide removal are discussed in the next section. Particular emphasis will be given to the identification of the required environmental factors.

8.0 BIOLOGICAL PROCESSES DEVELOPED AND TESTED TO-DATE

Laboratory and pilot plant studies of biological treatment processes for cyanide removal are summarized in this section. These include: trickling filters, activated sludge (with and without powdered activated carbon addition), extended aeration, fluidized beds, immobilized enzymes, and rotating biological contactors. Process variables, used in these treatability studies, are given in Tables B1 - B5 of Appendix B. It should be noted, however, that the efficiency of cyanide degradation in these processes is dependent upon the wastewater composition. Consequently, process parameters should not be directly compared for wastewaters of different origins.

8.1 Trickling Filters

Cyanide destruction by Actinomycetaceae in trickling filters has been studied using both simple cyanides such as NaCN, HCN, and KCN (Gurnham, 1955; Pettet and Mills, 1954; Porter, 1960; and Brink, 1960), and metal cyanide complexes (Gurnham, 1955; Winter, 1962; and Pettet and Mills, 1954). Cyanide concentrations above 2 mg/L adversely affected unacclimated filters initially, but the filter organisms demonstrated rapid recovery from shock loadings and, once acclimated to high cyanide concentrations, withstood up to 200 mg/L CN^- (Gurnham, 1955). Brink (1960) reported that supplementary sewage or substrate was necessary for successful trickling filter degradation of cyanide.

In filters acclimatized to cyanide, more than 99% of the cyanide was removed in solutions containing at least 100 mg/L of HCN as potassium cyanide or the complexes of zinc or cadmium (Pettet and Mills, 1954; Gurnham, 1955). Sewage was used as a supplemental feed.

Approximately 50% of the cyanide nitrogen appeared in the effluent as ammonia, nitrite, or nitrate. In the absence of sewage or other organic matter, degradation proceeded slightly less efficiently (97%). Eighty to ninety percent of the nitrogen appeared in the filter effluents, principally as nitrate, but partly as ammonia and nitrite. This proved that volatilization (see section 9.3) alone was not responsible for this disappearance, but that it should be attributed to biological oxidation.

8.2 Activated Sludge

Results of activated sludge studies are similar to those reported for trickling filters. When fed with sewage, cyanide concentrations up to 50 mg/L have been tolerated by activated sludge systems (Ludzack, et al., 1960; Fujii, et al., 1973; Kato, et al., 1976), and again, the presence of heavy metals or other substrate greatly influenced the tolerance limit. Kostenbadner (1969) reported on the treatment of coke oven wastes which contained ammonia, phenol, and thiocyanates in addition to cyanide. Phenol degradation in the systems exceeded 99%, but cyanide and thiocyanate degradation varied considerably (from 10-99%). Inhibition occurred when the ammonia concentration exceeded 2000 mg/L. Catchpole and Cooper (1972) studied the effects of adding certain "growth factors" to thiocyanate and cyanide containing wastes. Several amino acids, p-aminobenzoic acid, puruvic acid and D-glucose added to the wastes in concentrations below 5 mg/L significantly reduced the retention time required for cyanide and thiocyanate reduction. When glucose concentrations exceeding 50 mg/L were added to wastes with influent cyanide concentrations of 200

mg/L and thiocyanate concentrations of 500 mg/L (as NH_4CNS), a gelatinous sludge developed (due to the formation of cyanohydrin polymers) which interfered with treatment. Wong-Chong and Hall (1980) showed in a study on the treatability of coke-plant wastewater, that both ammonia (about 200 mg/L) and free cyanide (40 mg/L) could be treated, at least for a brief period, in a single stage system. Luthy et al. (1981) showed that influent cyanide levels of 100 mg/L could be removed in a biological reactor receiving coal gasification wastewater diluted to one-third of the original strength and pre-treated by lime aeration to strip ammonia.

Murphy and Nesbitt (1964) investigated the effects of carbon source and sludge wasting on the biological treatment of a synthetic potassium cyanide wastewater. In general, cyanide removal was poor using acetate as substrate, and the system was sensitive to loading changes. Using a synthetic sewage prepared from fish food, however, a much better cyanide removal was obtained. Sodium hydroxide was added to the feed tank to prevent loss of cyanide due to volatilization. However, the addition of NaOH permits larger concentrations of free ammonia, which inhibits nitrification. Cyanide was converted to ammonia, then nitrite and nitrate. Failure of the system was preceded by an increase in effluent ammonia and nitrite concentrations. A separate study using $K^{14}CN$ indicated that some of the cyanide was being metabolized to $^{14}CO_2$. Overall radioactivity recovery for the experiment was 72.5%.

8.3 Extended Aeration

Gaudy et al. (1982), in a laboratory study of an extended aeration modification of the activated sludge process, found that steady feeding of cyanide at concentrations of 10,15,20 mg/L, with a readily biodegradable substrate (glucose), resulted in excellent biodegradation and nitrification. However, even step increases in cyanide concentration of only 5 mg/L resulted in severe disturbances in the process response. Gaudy showed some specific characteristics of the microflora responsible for cyanide degradation (very slow growth but quite rapid degradation of CN^-), and indicated that the predominant heterotrophs in the biomass did not metabolize cyanide. Stripping of cyanide from the studied models was quite excessive (see section 9.3).

8.4 Activated Sludge Reactors with Powdered Activated Carbon Addition

Ford and Eckenfelder (1980) presented a comprehensive literature review, regarding the use of powdered activated carbon (PAC) in the activated sludge process, for several industrial wastewaters (municipal sewage, petroleum refineries, textile manufacturers and chemical processors). In general, the addition of PAC is reported to improve the operating characteristics of the activated sludge reactor by improving sludge settleability and by reducing sludge bulking (Robertaccio, 1977).

Enhanced nitrification of steel industry wastewaters, by the addition of PAC to activated sludge reactors, has been reported by several investigators (Bridle, 1980; Medwith and Lefelhocz, 1981). Two

mechanisms have been proposed to account for the improved performance. Nitrifiers may cluster on the PAC particles in a "fixed-film reactor" mode, permitting a larger percentage of the nitrifying bacteria to be retained in the biological system. In addition, it has been hypothesized that the PAC may adsorb organic compounds which are inhibitory to the nitrification process (Catchpole and Cooper, 1972; Beccaro et al., 1978; Bridle, 1980).

Evidence that PAC may act as a weighting agent has been obtained by Medwith and Lefelhocz (1981). Two biological treatment systems for ammonia removal from coke plant wastewater were investigated: (1) a rotating biological contactor; and (2) a suspended growth system. Both systems were evaluated with and without PAC. Degradation of ammonia was substantially improved in the systems utilizing PAC. Two nonadsorptive materials, coke breeze and coal dust, were evaluated as substitutes for activated carbon and similar results were obtained. This supported their conclusion that the carbon acted as a weighting agent.

Bridle et al. (1980, 1981) operated bench scale activated sludge reactors in the pre-denitrification nitrification mode at high solid retention times and hydraulic retention times and with PAC addition. They showed that most organics present in coke plant wastewater were effectively removed from the aqueous phase. However, accumulation of polyaromatic hydrocarbons, notably indeno-pyrene, naphthalene, pyrene and benzo-(a)-anthracene, occurred in the biological sludge. Also, heterocyclic nitrogenous compounds such as 9H carbazole, 9H anthracene carbonitrile, indolizene and phenanthridine were concentrated in the sludge. Any enhancement of

trace organic pollutant removal as a result of PAC addition, however, could not be assessed in their work.

The use of PAC in biological treatment systems, specifically for the removal of cyanides, has not been reported. Since the degree of removal by adsorption is highly dependent upon the substrate, adsorption isotherms are useful in determining if adsorption may contribute to the overall removal of the selected inorganic constituent. Adsorption of free and complexed cyanides has been studied by Huff and Bigger (1980), Saito (1984) and Manktelow et al. (1984). These studies have shown that activated carbon adsorbs complexed cyanides but has almost no affinity for free cyanide (Ingles, 1981).

In conclusion, the addition of PAC to activated sludge reactors may be valuable in the treatment of cyanide bearing wastewaters. Evidence suggests that the activated carbon may be utilized as a weighting agent and that moderate to stable metal cyanide complexes, may be adsorbed. Further developmental work is required to verify the possibilities.

8.5 Two-Stage Treatment - Activated Sludge Combined with a Biological Filter

At Brymbo Steel Works, England, a two-stage biological system was selected for the treatment of blast furnace blow down water after extensive pilot plant studies (Jackson and Kennedy,1978). Preliminary clarification of the effluents was accomplished by the addition of lime (to adjust the pH to 8.3) along with the addition of a polyelectrolyte. The effluents contained, on average, 77 mg/L of

suspended solids, 28 mg/L ammonia, 1.2 mg/L of cyanide, 2.5 mg/L of phenol, 2.8 mg/L of zinc, 20 mg/L of oil. The first stage of treatment (activated sludge) was designed to remove cyanide, phenol and toxic metals. The second stage (biological filtration) was designed to remove ammonia. The separation steps after the first and second stage of treatment were achieved by flotation, and the wastewater was enriched in phosphate to facilitate biological treatment in the first and the second stage. The wastewater retention in the activated sludge unit was about 10 hours (for maximal flow of 38 L/s the retention time was 7.5 hours) and the mixed liquor suspended solids level was stabilized at 1000 mg/L. The biological filter utilized blast furnace slag as a medium and had a diameter of 21 m.

The treatment provided for a cyanide removal to 0.05 mg/L, phenols to 0.1-0.2 mg/L, and ammonia to 1-2 mg/L (during winter operation). In the pilot plant trials, the concentrations of toxic material in the activated sludge tank were sufficiently high to inhibit the biological oxidation to ammonia and therefore, a biological filter was included in the plant solely to remove ammonia. However, in the full-scale plant, the activated sludge tank gradually acclimatized itself to the removal of ammonia in the presence of cyanide and phenol.

The main toxic metal of concern was zinc. Although the clarifier was intended to remove the majority of the toxic metals, some of these metals were in the form of complexed ions with cyanide and ammonia and remained in solution in the clarifier(pH 8.3).

Jackson and Kennedy concluded in the study that only very severe shock loads detrimentally affected the performance of the process. Acclimatization was very slow and ammonia reduction in the activated sludge tank was very susceptable to shock loads. It was not possible to conclusively demonstrate the need for an additional biological filter to remove ammonia.

8.6 Fluidized Bed Reactors

The fluidized bed process is a modification of the more conventional fixed film processes, such as the trickling filter, in which wastewater is passed upward through a bed of granular support media, typically sand, at a sufficient velocity to expand or fluidize the media. The granular media provides a large surface area for the establisnment of a biological film. The pilot-scale investigations of the biological fluidized bed process, conducted at the Wastewater Technology Centre (WTC), have shown this fixed film system to offer significant advantages in terms of reduced reactor volumes due to the high biomass concentration which can be maintained on the fluidized support media. The large surface area available for biological growth allows volatile solids concentrations in the bed to be maintained in the range of 10,000-20,000 mg/L.

Environment Canada initiated work in 1980, to examine the feasibility of applying pre-denitrification nitrification technology for the treatment of coke plant wastewater in a fluidized bed. The pilot-scale system at the WTC consisted of two fluidized bed reactors in series, coupled to provide carbon oxidation, nitrification and denitrification in the pre-denitrification operating mode. In this

flow configuration, the supplemental carbon requirements for denitrification are minimized as the organic carbon in the raw wastewater provides the energy source and serves as the electron donor for the denitrification reaction. Oxidizable nitrogen loading to the nitrification reactor (g NH_3-N.g $BVS^{-1}.d^{-1}$) had been defined as the critical process control parameter.

In the first phase of the fluidized bed work, 18 month pilot-scale trials of a two-stage fluidized bed system achieved a performance comparable to the suspended growth system examined by Bridle et al. (1980, 1981) but at the significantly reduced reactor hydraulic retention time of 16 h (Nutt et al., 1981, 1982a). In contrast, long hydraulic retention times (up to 60 h) and stringent solids retention time (SRT) control, in conjuction with wastewater dilution or powdered activated carbon addition, were required to ensure consistent performance using the activated sludge process. The pre-denitrification operating mode reduced the theoretical oxygen demand of the wastewater by approximately 66 percent due to the anoxic removal of a large fraction of the wastewater organics. The coupled fluidized bed system was capable of consistently achieving greater than 90 percent of total nitrogen removal from undiluted coke plant wastewater under steady and non-steady state conditions. Removal of other conventional contaminants including filterable organic carbon, phenolic compounds and thiocyanate exceeded ninety percent consistently at these operating conditions. The total cyanide content of the coke plant wastewater was reduced to 6.1 ± 1.35 mg/L from a median value of 8.0 ± 1.44 mg/L; however, the concentration of cyanide

compounds amenable to chlorination in the treated effluent was reduced to the detection limit (0.01 mg/L).

In Phase 2, the treatment of a mixture of coke plant wastewater and blast furnace blowdown water was examined over a six-month period (Nutt et al., 1982b, Nutt et al., 1984). Performance data, comparable to Phase 1, were achieved but at the considerably reduced hydraulic retention time of 4.5 h. Operation of the denitrification reactor at long solid retention times (in excess of 30 days) resulted in the accumulation of inorganic deposits of tetrabasic calcium phosphate which inhibited bed expansion and SRT control. At higher growth rates (lower SRT), these problems were eliminated. Flow distribution was a critical factor in achieving high biomass concentrations in the nitrification reactor. Removal of total cyanide was highly variable and depended upon the fraction of the total cyanide in the wastewater which was biodegradable. Total cyanide levels were reduced to 0.8 ± 0.9 mg/L from a median value of 1.8 ± 1.3 mg/L. Fluidized bed studies, utilizing cyanide bearing wastewaters from other industrial sources, have not been reported to date.

8.7 Immobilised Enzymes in Column Reactors

An interesting approach for cyanide removal from wastewater was developed by Kawai et al. (cited by Chibata,1978) which involves immobilisation of fungi, containing a cyanide decomposing enzyme, formamide hydrolyase. The latter is inducible on pre-exposure of the mycelia to low concentrations of cyanide. Nazly and Knowles (1981) extended this work and showed that Stemphylium loti could be

FIGURE 8.7.1 a

(Data of Nazly et al., 1983)

pH PROFILES FOR NON-IMMOBILISED (O) AND IMMOBILISED (●) CYANIDE HYDRATASE ACTIVITIES IN S. LOTI MYCELIA.

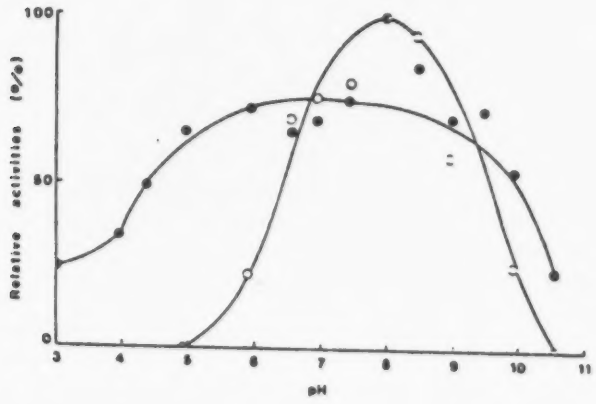
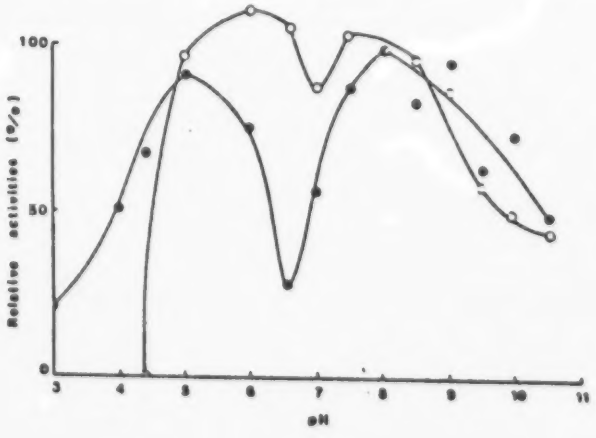


FIGURE 8.7.1 b

pH PROFILES FOR NON-IMMOBILSED (O) AND IMMOBILISED (●) CYANIDE HYDRATASE ACTIVITIES IN G.SORGHI MYCELIA.



immobilised and used to continuously convert cyanide to the less toxic product, formamide.

Cyanide detoxification in column reactors by immobilised Stemphylium loti, Gloeocercospora sorghi, and Fusarium moniliforme was studied by Nazly et al., (1983). Mycelia were immobilised using polyelectrolyte flocculating agents, 2% (w/v) each of Primafloc C7 and A10 (Rohm and Haas (UK) Ltd, Croydon), at pH 7.0. The effect of immobilisation on the enzymic properties of S. loti and G. sorghi were investigated. The apparent K_m values increased from 21.0 mmol and 25.5 mmol KCN to 43.5 mmol and 71.0 mmol KCN, respectively. Upon immobilisation for both of the fungal enzymes, the pH profile of enzyme activity widened. Two pH optima were observed for formamide hydrolyase of immobilised and non-immobilised G. sorghi, at about pH 6.0 and 8.0 respectively (see Figure 8.7.1).

The stoichiometry of 1:1 cyanide utilisation to formamide formation was retained on immobilisation, with complete conversion of 70 mmol KCN in 120 minutes by 0.12 g dry weight of S. loti and in 6 minutes by 0.13 g dry weight of G. sorghi. When the two fungi were stabilised by immobilisation, and tested in column reactors containing 1.2 g dry weight of S. loti and 1.3 g dry weight of G. sorghi, they completely converted cyanide (70 mmol; added continuously at 7.5 mL/h) into formamide for 2 days and 30 days, respectively. Stability was enhanced by inclusion of 1.0 mmol glucose in the 70 mmol KCN solution, by a further 10 h for S. loti and and extra 10 days for G. sorghi. Operational stabilities of immobilised G. sorghi (1.3 g dry weight) and F. moniliforme (1.0 g wet weight) in column reactors, with 100 % cyanide conversion, at varying flow rates was investigated.

G. sorghi was stable for 15, 10, and 2 days, whereas F. moniliforme was only stable for 48, 20 and 10 h at 30, 60 and 120 mL/ h flow rates, respectively.

Imperial Chemical Industries PLC (Billingham, Cleveland, U.K.) have patented this process (Beardsmore et al., 1982) and are presently investigating the technology at pilot scale. The immobilised enzymes are available in powder form for batch treatment and as immobilized pellets for column or fluidized bed reactors. The process characteristics (Powell, 1983) are listed below:

i) The enzyme can convert over one hundred times its weight of cyanide before the rate of conversion becomes uneconomic. Initial concentrations in the order of 8000 ppm can be reduced to less than 1 ppm, particularly in multi-stage operation, but the process is slower than treatment with hypochlorite.

ii) The enzyme functions between pH 5 and pH 10.5, optimally between pH 5.5 and pH 9.

iii) Many forms of waste can be treated, but the enzyme will not decompose the very stable metal complexes such as those of iron, copper and nickel.

iv) The manufacturer claims that treatment will usually be cheaper than conventional treatment.

8.8 Rotating Biological Contactor

According to the data presented by Mudder and Whitlock (1983), biological treatment of mine/tailings impoundment cyanide wastewaters has proved successful in the Homestake Mining Company. A

TABLE 8.8.1

HOMESTAKE GOLD MILL WASTEWATER CHARACTERISTICS (IN MG/L)

Parameter	Mine Water	Tailings Impoundment Water	Combined Wastewater
Thiocyanate	1.0-16.0	110.0-240.0	60.0±10.0
Total Cyanide	0.10-0.50	7.00-30.00	6.5±2.10
Method-c Cyanide	0.02-0.10	4.00-20.00	4.10±1.3
Iron	0.10-10.00	1.50-6.00	-
Copper	0.07-1.60	1.40-6.00	1.00±0.4
Nickel	0.01-0.04	0.20-0.40	-
Zinc	0.01-0.10	0.01-1.50	-
Ammonia-N	5.0-6.0	<1.0	6.00±1.0
Phosphorous-P	Trace	Trace	-
pH	5.0-6.5	7.00-9.5	-
Temperature(°F)	70-85	34-70	50-75*

* The temperature of the combined wastewater was seasonally variable but was not allowed to drop below 50°F in the winter. (Taken from Mudder and Whitlock, 1983)

combined stream of mine water and tailings impoundment water was used for the pilot plant studies. The volumetric ratio of these two streams varied from a 70/30 mine/tailings impoundment wastewater ratio in the winter, to a 50/50 mine/tailings impoundment wastewater ratio in the summer. The feed ratio was controlled by monitoring the inlet thiocyanate concentration. Compositions of these wastewater streams (in mg/L) are given in Table 8.8.1.

Both suspended growth and attached growth processes were evaluated with and without supplemental carbon sources (raw sewage). The processes included activated sludge, trickling filters (rock and plastic media), biological towers, aerated biological filters (EIMCO BAF process), and rotating biological contactors. A summary of the pilot plants tested is given in Table 8.8.2. Mudder and Whitlock commented that supplemental organic carbon sources were not required for the biological degradation of free and complexed cyanides since the wastewater contained sufficient dissolved organic matter for the growth of the flora (Mudder and Whitlock, 1984b, 1984c). However, the addition of an inorganic carbon source (soda ash) was found to aid nitrification.

All the attached growth processes yielded good to high quality low toxicity effluents but the RBC's superior performance coupled with the cost effective design and low operating costs made it the process of choice. The use of a fixed film process is certainly justified since such systems promote the growth of microorganisms, help to maintain their inventory in the treatment units, and are perhaps more resistant to wastewater toxicity. Although the activated sludge process originally exhibited the highest degree of treatment

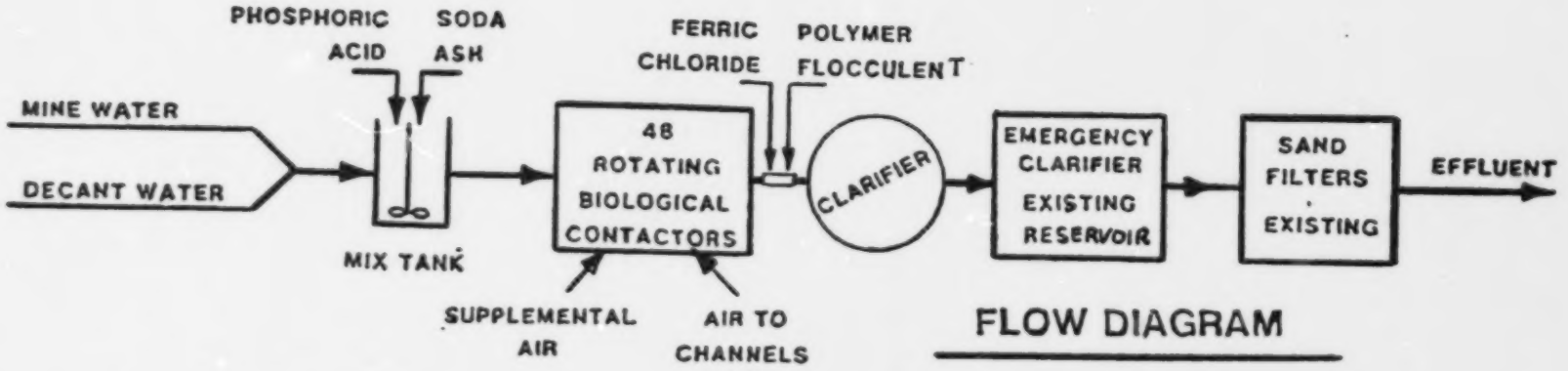
TABLE 8.8.2

SUMMARY OF BIOLOGICAL TREATMENT PROCESSES INVESTIGATED AT HOMESTAKE GOLD MINES

Parameter	Thiocyanate	Total Cyanide	Method-C Cyanide	Ammonia	Copper	Comment
Pilot plant influent (mg/l)	60.0 ± 10.0	6.50 ± 2.10	4.10 ± 1.30	6.0 ± 1.0	1.00 ± .40	The pilot plant influent is varied throughout the year from ratio of 70/30 mine/decant (tailings impoundment) wastewater in winter to 50/50 mine/decant wastewater ratio in the summer. The pollutant concentrations are highest in the winter with temperatures falling to 50 F in the wastewater.
2.0 meter RBC pilot plant effluent (mg/l)	<1.0	.35 ± .10	.05 ± .02	<.50	.04 ± .02	The pilot plants were furnished by Envirex. The original feasibility study was undertaken with the use of a .5 meter RBC pilot plant. The 2.0 meter pilot plant was operated with the first and second stages unbaffled. Supplemental aeration was fed to each stage of the pilot plant at an equivalent rate of 150 scfm (2.5 scfm actual). Stripping of biomass required 600 scfm. The total surface area of the pilot plant was 8,000 ft^2. The pilot plant was operated at flow rates of 2.0–8.0 gpm (.40–1.40 gpm/ft^2). Effluent values recorded in this table were obtained on clarified and sand filtered effluent. The rate controlling oxidation in the overall design was nitrification.
Laboratory bench scale activated sludge (mg/l)	<1.0	.27 ± .27	.06 ± .06	—	.35 ± .12	The bench scale reactors consisted of 5 liter plexiglass cylinders operated on a 24 hr. draw and fill cycle. Sludge ages examined ranged from 10 to 40 days. Activated sludge from the local sewage treatment plant was utilized for the initial biomass along with microbial seed from Homestake sources. Eventually aeration periods from 6–24 hrs. were examined. The system failed at 60 days due to metals toxicity.
22 foot biotower (mg/l)	<1.0	.87 ± .30	.08 ± .04	—	.10 ± .04	The pilot plant consisted of a 2 ft diameter steel pipe 22 feet in height packed with KORO-Z plastic media supplied by B.F. Goodrich Company. Maximum flow rate achieved was .25 gpm/ft^2 with .25 gpm/ft^2 recycle flow. Supplemental air was provided counter current to the gravity wastewater flow. Nitrification data is not meaningful as soda ash was not added to the raw wastewater feeding into the biotower. Trickling filters were also examined. The pilot plants consisted of two six foot 6" dia. plexiglass columns operated in series at flow rates similar to those of the biotower. The trickling filters were either packed with 5/8" Pall rings or crushed rock (1/2" dia.). The performance of the trickling filters was slightly less than the biotower.
Biological aerated filter (BAF Process) (mg/l)	<1.0	1.00 ± .60	.60 ± .02	1.2 ± .7	.03 ± .03	The pilot plant was supplied by EIMCO. The pilot plant consisted of two 1 ft. dia. plexiglass columns operated in series containing 6 feet of their patented media. The columns were operated in parallel and in series. The data presented in this table was from the series operation. Hydraulic flow rates were varied from .40–1.50 gpm/ft^2. Supplemental aeration was added counter current to the gravity wastewater flow in flows varying from .3–.5 scfm/ft^2.

FIGURE 8.8.2

FLOW DIAGRAM OF HOMESTAKE MINING BIOLOGICAL TREATMENT PROCESS



(MUDDER AND WHITLOCK, 1983)

efficiency with regards to total and method-c cyanide removal, Mudder and Whitlock reported that the system failed at 60 days due to slow microbial growth (evidenced by long sludge ages (>20 days)), coupled with the accumulation of toxic metals within the biomass. Modification of the process to include pre-treatment for metals removal would be required to yield a viable process.

Figure 8.8.2 depicts the Homestake RBC process. Within the RBC reactor, cyanides and thiocyanates are destroyed in the first stage, providing ammonia as an end product. The ammonia is subsequently oxidized to nitrate. Phosphoric acid is added to the feed as a trace nutrient, while sodium carbonate is used as a source of inorganic carbon for nitrification. Mudder and Whitlock indicated that the process removes both free and complexed cyanides including those of iron, and also removes toxic metals (principally copper) through biological oxidation and adsorption.

Table 8.8.1 illustrates that, with the exception of copper, the concentration of heavy metals in the Homestake plant were quite low. If the addition of soda ash to the wastewater also caused a sufficient increase of the wastewater pH, the toxicity of the copper species could be decreased substantially. Perhaps, copper-cyanide complexes could be partially absorbed on the biomass, or coprecipitated with iron salts and thus be removed with the excess biomass.

Three unique aspects of the Homestake site must be pointed out.

i) Mine water is available at a relatively constant temperature of 77±7°F. Thus, the wastewater does not need to be heated prior to treatment.

ii) The concentration ratio of approximately 10:1 SCN^- to CN^- is unique in comparison to the wastewater compositions encountered within the Canadian gold industry where typical ratios range from 0.2 - 10.0. A limitation may exist with regard to an optimum SCN^-/CN^- ratio for successful application of the RBC process. Since thiocyanate is more biodegradable than cyanide, an advantage possibly exists for wastewaters characterized by large SCN^- to CN^- ratios. Literature dealing with this subject is not currently available.

iii) Since the effluent is discharged to a recreational facility, stringent effluent guidelines (0.02 mg/L total cyanide) necessitated the development of a process with good CN^- removal efficiences.

The answers to the following questions would improve the understanding of the Homestake treatment concept:

i) What was the maintained pH of the treated wastewater?

ii) To what extent was the copper ionized in the wastewater?

iii) What were the copper and cyanide contents in the biomass?

iv) What are the predominant cyanide removal mechanisms (i.e. fractions volatilized, biodecomposed and sorbed in the treatment system)?

Although biodegradation of cyanidation wastewaters is not widely practiced in the mining industry, the literature indicates that biological oxidation of free cyanide, metal complexed cyanides, thiocyanates, and their breakdown products is possible. The relative merits and demerits of each biological process are discussed in Section 11.0 in order to select a candidate process for biodegradation studies for Canadian mining effluents. Before the discussion is completed, the mechanisms for cyanide removal in a biological reactor and the limitations of biological treatment will be considered.

9.0 CYANIDE REMOVAL MECHANISMS IN BIOLOGICAL TREATMENT SYSTEMS

In an aerated biological waste treatment system four interrelated mechanisms have been reported to contribute to the overall cyanide removal (Raef et al.1974, 1977a, 1977b):

i) Chemical reaction in solution with the substrate

ii) Adsorption onto biological floc

iii) Biological metabolism

iv) Stripping

The relative importance of each mechanism is summarized in the following discussion. It should be noted, however, that the contribution of each mechanism is dependent upon the biological system used. The following discussion is based on experimental data obtained using activated sludge and extended aeration systems. Data are not available for other biological processes.

9.1 Chemical Reaction of Cyanide in Solution with the Substrate

A supplemental carbon source, such as glucose, raw sewage or soluble fish food, is often fed to the biological oxidation units along with the cyanide. Glucose, for example, is known to react with cyanides to form cyanohydrins, which then hydrolyze to the corresponding aldonic acids (see Figure 9.1). Raef et al. (1974, 1977a, 1977b) studied the reaction of glucose with cyanide in sealed glass ampoules. Reaction rates were significant above pH 8.0. The reaction is pseudo-first order, with an optimum pH of 11.0. However, in an activated sludge system, this mechanism contributed to less than 15% of the overall cyanide removed.

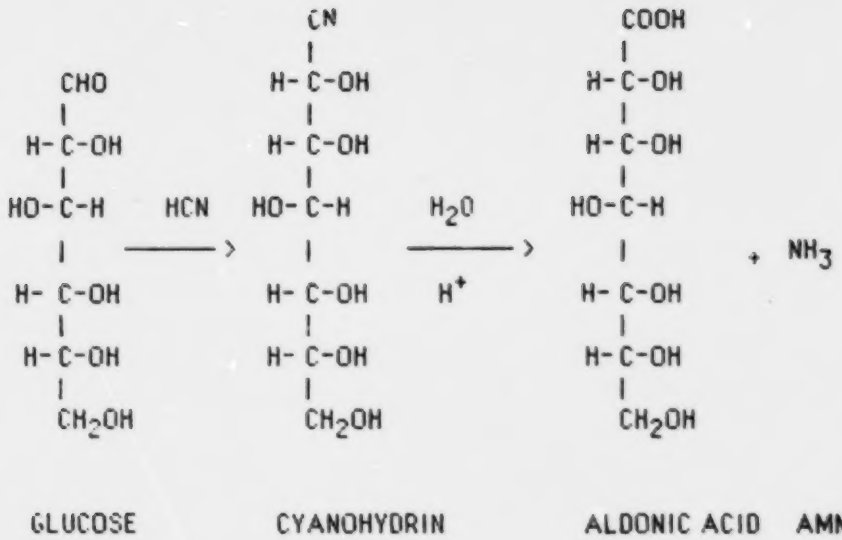


Figure 9.1: **Chemical Reaction Pathway of Cyanide with Glucose**

9.2 Adsorption of Cyanide onto the Biological Floc

Raef et al. (1977a) studied adsorption of cyanides on Bacillus megaterium and on heterogeneous cultures. Bacillus megaterium (ATCC Strain 2300), a nonflocculating culture of bacteria, did not significantly adsorb cyanide. On the other hand, adsorption accounted for 15 percent of the observed cyanide removal when heterogeneous flocculating bacteria were used. These differences were attributed to a large polysaccharide matrix, present in flocculating bacteria, which

greatly increases the relative number of adsorption sites (Raef et al., 1974). Although the extracellular composition of organisms affects adsorption, Raef concluded that this mechanism plays a minor role in overall cyanide removal in an aerated biological treatment process.

9.3 Stripping and Biological Metabolism

Tracer studies were conducted by Raef et al. (1977a, 1977b) to determine the relative importance of stripping and metabolism. Acclimated cultures of starved heterogeneous flocculent bacteria were batch-fed cyanide and glucose. At the completion of the experiment, washer solutions and the final reactor solutions were analyzed for $H^{14}CN$, $^{14}CO_2$ and ^{14}C incorporated into cellular material. A materials balance indicated approximately 95% recovery of radioactivity. The comparatively smaller quantity of $^{14}CO_2$ produced (see Table 9.1), suggested that ^{14}CN metabolism was not the major removal mechanism in an aerated biological treatment system. Stripping accounted for 60-90% of the cyanide removed, biological conversion to CO_2 accounted for 9-36% of the cyanide removed, and 1-10% of ^{14}C was found in the washed cells at the termination of the experiment. This ^{14}C was either adsorbed cyanide bound so tightly that washing did not remove it, or represented ^{14}C incorporated into cellular material.

TABLE 9.1

CARBON BALANCE IN AERATED BATCH CULTURES OF HETEROGENEOUS BACTERIA

Initial Biological Solids concentration	Percent of Recovered Carbon in Each form (%)		
mg/L	^{14}CN	$^{14}CO_2$	^{14}C cells
592	62.8	36.0	1.2
696	89.6	9.7	0.7
848	75.7	15.2	9.1
1963	74.5*	23.5	2.1
483	84.9*	8.8	6.3

* Assumes some CN in gas washer either polymerized or formed organic compounds when caustic was added.

(Taken from Raef et al., 1977b)

Observations of other investigators are highly variable. A study by Ludzack and Schaffer (1960), using an activated sludge system, indicated that stripping was not significant below cyanide concentrations of 60 mg/L. Similar results were obtained in another study by Harden, Jones and Gauthier (1983). Cyanide was completely metabolized below concentrations of 40 mg/L. At greater influent cyanide concentrations, stripping of cyanide was detected when the culture was acclimatized for a short time interval (32 days).

However, when the culture was acclimated for a longer time interval (190 days), cyanide concentrations, up to 200 mg/L, were completely metabolized. Nesbitt, Kohl and Wagner (1959) reported 97.9 % recovery of the cyanide carbon as CO_2 when no other source of carbon was available. Gaudy et al. (1982) have shown that up to 60% of the HCN is removed by air stripping in a single-stage extended aeration system. A synthetic feed, supplemented with 10-20 mg/L cyanide, was used. Organic substrates as well as ammonia and cyanide were effectively removed. Cyanide did not accumulate in the sludge.

A direct comparison of these studies cannot be made since the process variables, such as aeration rate, substrate concentration, type of biomass, etc. are not similar. Although stripping was the major removal mechanism in many studies, it appears that biological metabolism, may be the predominant mechanism if the process variables (aeration rate, cyanide loading, biomass concentration, etc.) are selected properly.

10.0 LIMITATIONS OF BIOLOGICAL DEGRADATION

10.1 Toxicities of Heavy Metals, Free and Complexed Cyanides in Biological Treatment Systems

The toxicities of the various metal cyanide complexes in biological treatment systems were investigated by Pettet and Mills (1954) and Gurham (1955). The observed trends were similar to those reported for the toxicities of metal cyanide complexes to fish (section 5.1). The toxic effect was mainly due to the presence of free cyanide ion; for complex cyanides, the effect was measured by the concentration of simple cyanide released by spontaneous breakdown. The stable complexes, such as ferrocyanides and nickelocyanides, had the least effect, whereas, less stable complexes, like copper and cadmium, were intermediate in their effects.

In order to distinguish the toxic effect caused by metallocyanides from the effect of simple heavy-metal ions, corresponding tests were run with the equivalent concentration of the heavy-metal sulfates (Gurnham, 1955). Trickling filter operation was not affected by these solutions. Many, but not all, of the heavy metals appeared in the effluent. Gurnham commented, however, that gradual build-up of metal in the filter slimes, over a prolonged period of time, would in all probability interfere with the filter operation.

Another study by Winter (1962), using plating wastes and synthetic waste fractions in trickling filters, indicated that the average levels of metals present in the waste were not markedly toxic to the organisms used (Norcardia). Although 50-100 per cent of the metals present in the influent wastes were deposited on the filters,

there was no apparent toxic effect shown during a three month study with blended wastes.

10.2 Type of Cyanide Degradable

The experimental data of most investigators indicate that the biodegradability of a given metal cyanide complex is related to the thermodynamic stability of the complex. In general, strongly bound metal cyanide complexes cannot be degraded, whereas, weak complexes and simple cyanides are readily degraded.

Pettet and Mills (1954) and Gurnham (1955) reported the degradation of complexed cyanides in trickling filters containing Actinomyces. At 100 mg/L cyanide, in the form of the simple potassium salt or the complex cyanides of zinc, cadmium, or copper, 99% of the cyanide was destroyed after proper acclimatization using sewage as a supplemental feed. Destruction of cyanide was less efficient with the ferrocyanide and nickelocyanide complexes.

In the absence of sewage or other organic matter, degradation proceeded slightly less efficiently. Potassium, zinc and cadmium cyanides were almost completely destroyed (97%) from feed liquors of 100 mg/L CN^-. Cuprocyanide and nickelocyanide complexes were destroyed to the extent of 75% or 80%. Ferrocyanides, however, were attacked only slightly; oxidation to ferricyanides occured in the filter.

Winter (1962) investigated the ability of Actinomycetaceae: Nocardia to degrade simple and complexed cyanides in trickling filters. The cultures achieved 90 per cent degradation of up to 100 ppm ionic cyanide, present as KCN, and 69-90 per cent degradation of

up to 20 ppm of complexed metal cyanides, present as plating waste or plating waste fractions.

Further supporting evidence is available in the biological treatment of photographic processing effluents. Free cyanide is not present in any of these wastewaters. Concentrations as great as 500 mg/L of ferrocyanide ion have passed through small laboratory scale activated sludge units without adverse effects (Dagon, 1973). However, these were indoor laboratory experiments where little decomposition to free cyanide would occur. Concentrations of 10 to 40 mg/L have been passed through an outdoor pilot plant unit without any apparent problems. In both cases ferrocyanide appeared to have no serious effect on the activated sludge system and passed through the treatment plant with little or no change.

More recent data, gathered with a rotating biological contactor (Mudder and Whitlock, 1984d), suggests that heavy metal cyanide complexes (principally iron and copper) may be removed through adsorption onto the biomass. Thus a potential method of removing strongly bound metal cyanide complexes may exist, at least for wastewaters containing small amounts of these complexes. It is difficult to extrapolate this finding to wastewaters composed of very stable metal cyanide complexes with the limited amount of data gathered to date. Therefore, it would be prudent to avoid the use of potlining leach liquors and base metal sulfide flotation tailings for biological treatment studies.

10.3 Wastewater Strength

It is difficult to recommend a range of suitable cyanide feed concentrations for effective biological degradation, given the limited amount of data published in the literature. Specific efforts were not made in most investigations to determine the maximum loading rates permitted. In studies of activated sludge systems, cyanide concentrations, ranging from 10 - 50 ppm (Fugii, 1973; Kato, 1976; Wong-Chong and Hall, 1980) to 100 - 200 ppm (Luthy et al., 1981; Harden Jones and Gauthier, 1983), have been used. Free cyanide degradation efficiencies exceeded 99% in these studies. Concentrations as high as 200 mg/L cyanide were used by Pettet and Mills (1954) in trickling filter studies; in filters acclimatized to concentrations of at least 100 ppm of HCN, cyanide degradation exceeded 99%. Mudder and Whitlock (1983, 1984) utilized cyanide concentrations in the range of 1 - 10 ppm in degradation studies of gold mill effluents. The majority of work has been done with effluents containing less than 200 mg/L cyanide, which suggests that this may be the practical upper limit. Further experimental evidence is required to verify this hypothesis. The focus of the remaining discussion is the selection of a suitable gold mill wastewater stream for biodegradation studies.

10.4 Selection of a Wastewater Stream for Biodegradation Studies

The tailings impoundment water appeared to be the most suitable candidate for biological treatment studies. Barren bleed and tailings repulp were judged to be unsuitable for the reasons given below:

i) Barren bleed streams (40 - 700 ppm cyanide) are probably too concentrated to be used as feed for a biological wastewater treatment plant.

ii) The tailings repulp slurry (13 - 280 ppm cyanide) may be within the range of interest for biological treatment, but solids removal would be necessary.

iii) Both streams are used in a typical gold mill to transport waste solid materials to the holding ponds.

iv) The pond is a cost effective method for removing the bulk of the cyanide through natural degradation.

One disadvantage of treating the tailings impoundment wastewater at Canadian gold mills, are the freezing water temperatures during winter. Homestake (Lead, SD) has solved this problem by combining the pond effluent with warm minewater (available at 75°F) to provide sufficient temperatures (> 10°C) to sustain effective biological process rates. In Canada, minewater temperatures are, in general, much colder (10 to 16 °C) since the mines are shallow (Gordon Ritcey, private communication). Typical minewater temperatures are given in Table 10.1. In order for a biological cyanide removal process to become competitive with physical/chemical treatment methods at Canadian mills, methods of sustaining effective biological process rates would have to be established. The options may include one or more of the following:

i) Sufficient volumes of warm water mill streams would have to be located. Candidates include minewater, barren bleed, process steam condensate, cooling tower water, and bioplant

TABLE 10.1

TYPICAL MINE WATER TEMPERATURE* IN ONTARIO MINES

Mine	Temp. (°C)
Inco Mines Ltd. Copper Cliff South	16
Inco Mines Ltd. Creighton #9 (7,000 ft. deep)	14
Inco Mines Ltd. Frood - Stobie Mine	12-14
Inco Mines Ltd. Levack	16
Denison Mines Ltd.	8 (minimum)

* Minewater temperatures are a function of the depth of the mine; deeper mines have warmer minewaters.

effluent. These streams may be used as dilution waters or heat exchanger fluids.

ii) Deliberate heating of the wastewater stream could be considered as part of an economic analysis if sufficient warmwater sources could not be located.

iii) It may be possible to isolate a local mutant strain of bacterium which is able to thrive under colder process temperatures.

iv) A deep pond could be used to store the barren. This would in all probability involve a trade-off since natural degradation would be less effective.

11.0 EVALUATION AND SELECTION OF PROMISING BIOLOGICAL PROCESSES

11.1 Evaluation of Promising Biological Processes

The biological wastewater treatment processes for the destruction of cyanide identified in Section 8.0 as promising technologies were:

- the activated sludge process
- the activated sludge/powdered activated carbon process
- the extended aeration process
- the fluidized bed process
- the trickling filter process
- the rotating biological contractor process
- the immobilized fungi process

There is evidence, some of which is circumstantial, to suggest that all of the aforementioned processes have the capability to bring about the destruction of cyanide in various mineral processing effluents and thus to produce effluents which meet discharge guidelines. The following outlines the rationale for deciding which biological wastewater treatment process to recommend for further investigation in Canada.

The decision analysis protocol comprised two stages. In the first stage, general screening criteria were defined and a comparison made between these and performance characteristics for all seven processes. Those biological processes which proved unable to meet these criteria were rejected from further consideration. In the second stage, specific evaluation criteria were defined and a comparison made between these and the anticipated performance

capabilities of those processes which passed the first stage screening.

11.1.1 General Screening Criteria

The screening criteria defined included the following:

- Ability of process to biodegrade cyanide.
- Ability of process to produce an effluent which satisfies Canadian regulations and guidelines.
- Suitability of process to Canadian conditions.
- An adequate level of technological process development.
- Sufficiency of treatability data obtained on actual wastewaters in continuous testing.

The determination of whether a process met the screening criteria necessarily involved a considered judgment based on all available information rather than quantification, since quantification often proved impossible. The results of screening in this manner are presented in the Decision Criteria - Process Performance Comparison Matrix. An examination of this matrix reveals that the processes passing the screening included all those considered with the exception of the immobilized fungi process.

11.1.2 Specific Evaluation Criteria

The specific evaluation criteria defined included the following:

- Ability of the process to deal with complex cyanides.

TABLE 11.1

DECISION CRITERIA - PROCESS PERFORMANCE COMPARISION MATRIX

		Activated Sludge	AS-AC	Extended Aeration	Fluidized Bed	Trickling Filter	RBC	Immobilized Fungi
General Screening Criteria	Capability of process to degrade cyanide	yes	yes	yes	yes	yes	yes	yes
	Ability to meet regulations/guidelines	yes	yes	yes	yes	yes	yes	yes
	Suitable to Canadian conditions	yes	yes	yes	yes	no	yes	yes
	Adequate technology development	somewhat	no	no	somewhat	somewhat	somewhat	no
	Sufficient treatability data available - Lab - Pilot - Full scale	 yes no no	 some no no	 yes no no	 - some no	 - some no	 - some no	 some no no
Specific Evaluation Criteria	Ability to deal with complex cyanides	no	probably	no	no	no	no	no
	Ability to tolerate variable flow	yes	yes	yes	unknown	unknown	unknown	yes
	Ability to tolerate variable loading	2 X normal	2X normal	2 X normal	unknown 2X normal	unknown 2X normal	unknown 2X normal	yes
	Maximum cyanide removal	complete	unknown; should be complete	complete	complete	99%	95%+	complete
	Maximum initial cyanide concentration allowed	5 mg CN/g MLVSS/hr	unknown, should be about same as activated sludge	5 mg CN/g MLVSS/hr	9ppm	200ppm	6ppm	1400 mg CN/g
	Process operating temperature	25-30°C	25-30°C	25-30°C	25-30°C	25-30°C	25-30°C	25-30°C
	Minimum HRT	2.2 hr	unknown, probably very reliable	22.5 hr	16 hr	60 gal/cuyd/d	0.5 gpd/ft^2	unknown; should be 10 min
	Process reliability	somewhat reliable	unknown, probably very reliable	somewhat reliable	reliable	reliable	reliable	very reliable
	Degree of skill required to operate	average	average	average	average	average	simple to average	average
	Possibility of long process SRT	good	better	better	best	best	best	best
	Process economics	requires compressed air; thus moderately costly	similar to AS plus carbon replacement or regeneration required, thus more than moderately costly.	requires compressed air and extensive insulation; thus costly	most expensive due to large volume of water needed to recirculate and to suspend media	air blower not required; thus near lower cost end	low power required to rotate discs; thus near lower cost end	fungi replacement required; thus more than moderately costly

TABLE 11.1 (CONT'D)

	Activated Sludge	AS-AC	Extended Aeration	Fluidized Bed	Trickling Filter	RBC	Immobilized Fungi
Comments	biomass difficult to settle; coagulants & flocculants may be required as a minimum to retain biomass	not enough work done to date, AC will degrade complex CH and weigh biomass thus easily retainable, past experience on toxic feeds shows advantage.	biomass very difficult to settle; coagulants & flocculants may be required as a minimum to retain biomass	biomass sloughing off media used to be settled and filtered.	biomass sloughing off media; needs to be settled and filtered	biomass sloughing off discs; needs to be settled and filtered	not enough work done to date; simple downflow operation independent of flow and concentration fluctuations; advantage in industrial application

- Ability of the process to tolerate influent flow variability.
- Ability of the process to tolerate variable loading.
- Maximum cyanide removal ability by the process.
- Maximum permissible initial cyanide concentration applied to the process.
- Common process operating temperatures.
- Minimum hydraulic retention time for the process.
- Process reliability.
- Degree of operational skill required by the process.
- Ability of the process to provide the required length of solids retention times.
- Process economics.

Unlike the case of the earlier general screening analysis, the determination of whether a process met the specific criteria involved quantitative comparison to a much greater degree. The results of comparisons with respect to the specific evaluation criteria are presented in the Decision Criteria - Process Performance Comparison Matrix. In order to better interpret the meaning of these comparisons, some general comments follow, regarding each process under consideration.

11.1.3 Activated Sludge Process (Complete-Mix)

The design considerations for the activated sludge process are rigorous and commonly include the following parameters:

- organic loading rate

- volumetric loading rate
- reactor solids concentration
- sludge return ratio
- oxygen requirements
- sludge production rate

The main advantage of the activated sludge process is that it produces an effluent of high quality at a reasonable cost. Furthermore, the process is controllable since, through adjustment of the amount of sludge wasted, the operator is able to regulate the SRT in order to obtain the desired effluent quality. Activated sludge processes are relatively resistant to shock loads and can achieve acceptable effluents in spite of dynamic inputs, although they do perform better under more stable conditions. Because of the small volumes associated with activated sludge reactors, there is only a small influence of atmospheric cooling and thus these types of reactors exhibit a relatively uniform temperature. If the temperature does change, the SRT may be adjusted to compensate for it. The complete-mix activated sludge process is popular in industrial waste treatment applications because of its resistance to toxic shock loads. Because the entire reactor contents are, theoretically, at the concentration of the effluent, this process is also well suited to the treatment of wastes which are toxic or inhibitory at high concentration. Because the microorganisms are never in contact with the concentrated waste, the toxic effects are minimized. The homogeneity of the tank contents also makes this process amenable to

automatic control of dissolved oxygen, pH and nutrient addition. Modular installation of the process is also an advantage.

The principal disadvantage associated with the activated sludge process is a direct result of its controllability; that is to say, it is a complicated process which requires relatively sophisticated operation in order to achieve the desired results. It is, however, relatively sluggisn in response to transient changes; a fact which limits the applicability of some automatic control techniques. The complete-mix activated sludge process has a tendency to produce sludge which settles more slowly than other process modifications. This disadvantage may be circumvented by appropriate design considerations. Capital and operating costs, although reasonable, are among the highest for biochemical operations, so that the decision to install an activated sludge system requires a considerable commitment on the part of an industry. The degree of this commitment has often not been recognized, with the result that most problems which are associated with the process are the direct result of inadequate operation.

11.1.4 The Activated Sludge/Powdered Activated Carbon Process

Because of the similarities between the complete-mix activated sludge process and the activated sludge/powdered activated carbon process, the design considerations, as well as the advantages and disadvantages, are substantially similar. The differences which do exist are a direct result of the requirement for fresh powdered activated carbon. Carbon is added continually to the aeration tank in

order to provide a degree of enhanced treatment through adsorption of both degradable and non-degradable organics.

The advantages of this process over the activated sludge process include an improved resistance to the adverse effects of transient loading and toxics, as well as improved sludge settleability. Overall, this process promises improved performance over that of activated sludge alone.

The disadvantages of the activated sludge/powdered activated carbon process over activated sludge include the difficulties in judging the level of biomass present and the differentiation between powdered activated carbon and biomass using standard tests. Another disadvantage is the accumulation of inerts in the sludge inventory at long SRT's. Finally, there is the additional cost to the process which is related to the regeneration or replacement of the powdered activated carbon.

11.1.5 The Extended Aeration Process

The advantages and disadvantages of the extended aeration process are generally similar to those identified for the activated sludge process. This similarity arises not only because the extended aeration process is a modification of the activated sludge process but also because a complete-mix reactor regime is often employed in extended aeration. In addition, the design considerations for extended aeration are similar to those for activated sludge.

The extended aeration modification was conceived originally to overcome two objections to activated sludge; namely: the large amount of waste sludge which must be disposed and the need for close

operational control of the process. A high degree of stabilization is attained in the process by virtue of the large reactor volume provided and the long SRT employed in order to permit degradation of the sludge produced. This high degree of stabilization and reduced sludge production is obtained at the expense of a high oxygen requirement and an effluent which sometimes contains a relatively higher concentration of suspended solids than would be expected from the activated sludge process. Economic considerations often limit the application of the extended aeration process to small facilities and low strength wastes.

11.1.6 The Fluidized Bed Process

The technology of the fluidized bed process is still in active development and thus, the related design considerations are not yet well established. However, it can be said that the following considerations are of importance:

- substrate loading rate
- hydraulic loading rate
- bed expansion
- recycle ratio
- carrier medium
- oxygen requirements
- sludge production rate

The reported advantages of the fluidized bed process are numerous. The very high biomass concentration and long SRT in this process enable hydraulic residence times of only a few minutes to bring about treatment effects which are comparable to those observed in

activated sludge processes having hydraulic residence times which are much longer. Also, the need for secondary sedimentation is eliminated or greatly reduced. Fluidized bed reactors are typically small and therefore land area requirements are reduced as are the associated capital costs.

However, several important technical problems with this system remain unresolved. There are reports that there is a carry-through of influent solids. Also, there is evidence that oxygen transfer is unsatisfactory and this situation necessitates the use of a high recycle ratio. Perhaps most importantly, the separation of biomass from the carrier medium is still very problematic.

11.1.7 The Trickling Filter Process

The design considerations for the trickling filter process are as follows:

- organic loading rate
- hydraulic loading rate
- recirculation ratio
- filter medium
- dosing interval
- sludge production rate

The principal advantage of trickling filters stems from their simplicity and ease of operation, thus making them ideal for remote sites. Futhermore, because large masses of organisms must be present to achieve effluents of high quality, the microorganisms possess substantial reserve capacities. Consequently, the biomass is

very tolerant to changes in the influent composition and flow rate. In addition, the dense nature of microbial films which slough from the medium, produces sludges of relatively constant character which can be readily removed by sedimentation. One advantage which has long been claimed for trickling filters is an ability to survive shock loads of toxics. However, this ability may not be a general characteristic but rather may be a function of the duration and intensity of the shock.

The factors responsible for the principal advantages of trickling filters are also the factors responsible for their principal disadvantages; that is to say, their simplicity and ease of operation. Because the microoganisms grow attached to a fixed surface, there is notning that can be done to alter their mass within the reactor in response to environmental changes and therefore, there is no effective way of controlling the process and tnus effluent quality. Consequently, if increases occur in the concentration or flowrate of the wastewater being treated, tne quality of the effluent will deteriorate. Likewise, if the temperature drops, the rate of substrate removal will also drop and tne effluent quality will suffer. Accordingly, large reactors are required to ensure the achievement of effluents containing low concentrations of residual substrate over a broad range of influent or environmental conditions. In addition to the aforementioned problems, icing during winter in northern climates can be a problem unless the filters are enclosed.

11.1.8 The Rotating Biological Contactor Process

The design considerations for the rotating biological contactor process are the same as those for the trickling filter process but with the addition of the following:

- peripheral velocity
- number of stages in series

Many of the advantages of rotating biological contactors are similar to those of a trickling filter but there are key differences which give the rotating biological contactor process important advantages. In rotating biological contactors, the biomass is passed through the wastewater rather than passing the wastewater over the biomass as in trickling filters. This ensures adequate wetting of all the organisms regardless of the influent flowrate, thus eliminating the need for recirculation. In addition, the intensity of contact between the biomass and the wastewater can be altered by simply adjusting the rotational speed of the discs, permitting direct control of the biofilm thickness. Adjustment of the rotational speed can also alter the rate of oxygen transfer, although supplemental aeration may still prove necessary. The recycle of solids in rotating biological contactors is not necessary; a fact which constitutes yet another advantage. Perhaps one of the major advantages associated with the rotating biological contactor is its low power requirements. The energy required to operate a rotating biological contactor is only a fraction of that required to operate an activated sludge process. Like a trickling filter, the claim is often made that a rotating biological contactor has a better shock load or transient state

response than activated sludge processes. This is true in the sense that toxic and other deleterious shock loads often pass through the reactor rapidly enough to avoid killing all the biomass so that recovery is fairly rapid. As far as simple quantitative changes in flow and concentration are concerned nowever, rotating biological contactors have been shown to be sensitive to these parameters. Furthermore, little reserve capacity is provided with which to minimize fluctuations in effluent quality. Thus, if stringent effluent quality criteria are to be met by a rotating biological contactor receiving a variable influent, either equalization or extra treatment capacity will likely be required to reduce the fluctuations in effluent quality and to ensure the desired level of treatment.

The principal disadvantages associated with the rotating biological contactor process are this lack of reserve capacity and the lack of operational controls. These disadvantages are offset somewhat by the modular nature of rotating biological contactor systems which makes the addition of new reactors, to increase flexibility, relatively easy. Another disadvantage of rotating biological contactors is that the rate of oxygen transfer from rotation of the discs places a limitation on how heavily the discs may be loaded. Finally, there is the disadvantage of climatic influences in which icing during winter may present a problem unless the reactors are enclosed with an insulating cover.

11.2 Selection of Promising Biological Process

Having due regard to the relative merits and demerits for each of the remaining candidate processes and from a consideration of

the Design Criteria - Process Performance Comparison Matrix, the following comments can be made.

In the case of each candidate process, there is insufficient published information on which to base design calculations. Therefore, laboratory and/or pilot scale testing is necessary for design purposes.

The activated sludge process suffers from the point of view of economics and complexity in operations and therefore it is considered prudent to reject this process from further consideration at this time. Similar comments can be made for the activated sludge/powdered/activated carbon process. The extended aeration process appears to be appealing with respect to lack of complexity, but the large volume requirements and the attendent mixed liquor cooling problems tend to detract from this appeal. Accordingly, further consideration of the extended aeration process is not justified. The fluidized bed process, being relatively new has many unresolved problems. The application of the process in this case, for a complex wastewater, is considered imprudent and therefore is not recommended. The trickling filter process holds definite promise but its space requirements and the icing aspect detract from its appeal. This process also should not be considered further. The rotating biological contactor process holds all the advantages of the trickling filter process and, in addition, has minimal space requirements, as well as proven engineering solutions to the icing problem. For these reasons, it is considered to be the process of choice.

12.0 PRE- AND POST-CHEMICAL TREATMENT

Three factors have contributed to a successful biotreatment plant at Homestake Gold Mines:

i) A dilute wastewater, tailings pond overflow (34-70°F) combined with mine water (70-85°F), is used as feed to the biotreatment plant. The warm minewater is used to maintain temperatures sufficiently warm (50-65°F) to sustain effective biological process rates. At these lower influent cyanide concentrations (4-10 ppm), the toxicity of the influent to the microorganisms is reduced and the amount of cyanide removed by metabolism is probably increased (see section 9.3).

ii) The wastewater contains considerably more SCN^- than CN^-. Thiocyanate is more biodegradable than cyanide. A method is described below which may be able to increase the SCN^-/CN^- ratio of a given wastewater stream.

iii) The wastewater contains relatively small amounts of strongly bound complexed cyanides. Only two complexed cyanides are of concern: copper and iron cyanides (see Table 8.8.1 of Section 8.8). The chemical post treatment methods, described below, may eliminate residual levels of these complexes from the final effluent.

12.1 Chemical Pretreatment

One chemical pretreatment method which may be used to increase the SCN^-/CN^- ratio, incorporates calcium polysulfide as a reagent (Ganczarczyk, 1984). The source of polysulfide-sulfur is a commercially available pesticide/fungicide called limesulfur. This

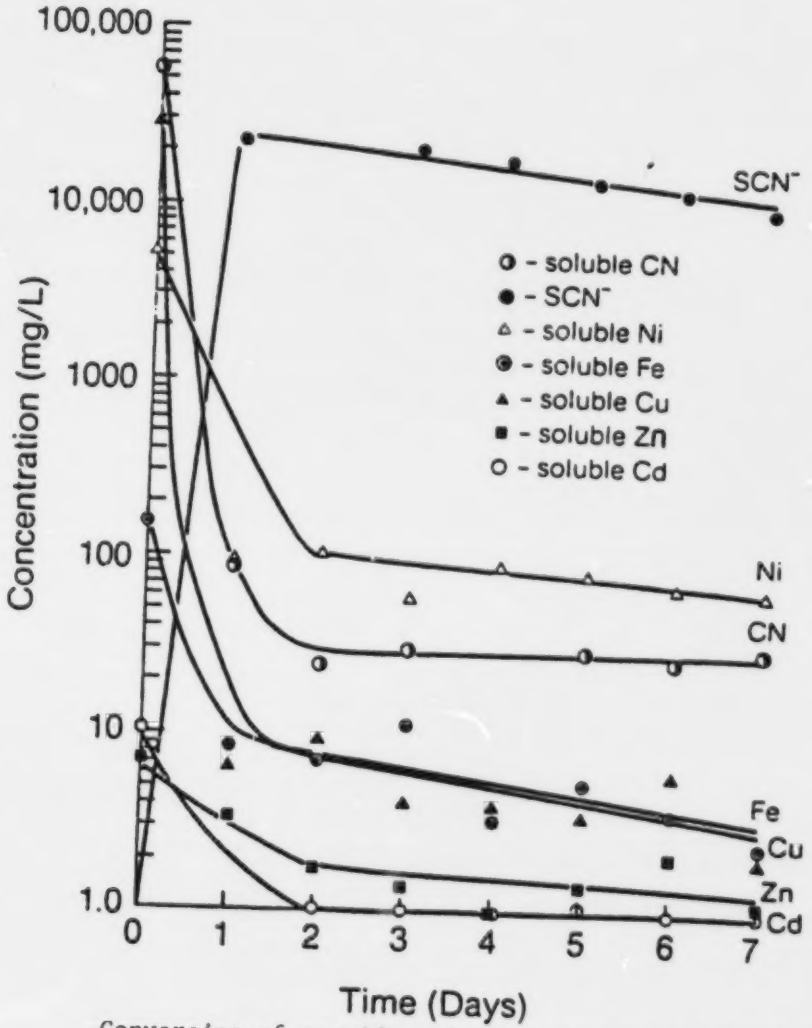
product can also be obtained by dissolving elemental sulfur in a hot suspension of lime in water. A typical cyanide conversion curve is illustrated in Figure 12.1 for a metal plating wastewater, containing an initial total cyanide level of 60,000 ppm (Ganczarczyk, 1984). To reduce the cyanide level to approximately 50 ppm, the required dosage of polysulfide is about 20 % higher than the stoichiometric requirements.

Polysulfide conversion also has the ability to remove complexed cyanides prior to biological treatment (refer to Figure 12.1). Heavy metal removal, including iron, copper, zinc and cadmium is observed for metal plating wastewaters, presumably by the dissociation of the metal-cyanide complexes, and the precipitation of ionized metals as sulfides (Ganczarczyk, 1984).

Polysulfide conversion of cyanide in gold mill wastewaters is currently under investigation (Zaidi, 1985a). The results of this study have not yet been released. Preliminary data indicate some promise for partial conversion of cyanide to thiocyanate in tailings impoundment wastewater. However, reaction rates for dilute wastewaters over extended periods of time (> 8 hrs) are not well defined. Additional data, which includes a sludge analysis, need to be gathered to determine the fate of the free and metal complex cyanides.

Although there are gaps in knowledge with respect to the overall efficiency of polysulfide addition to gold milling effluents, the approach appears to have great promise as a means of partial pretreatment to control both the CNS^-/CN^- ratio and to simultaneously reduce the concentration of complexed cyanides. By this means the

FIGURE 12.1



Conversion of cyanide and precipitation of metals in calcium polysulfide treatment of the stripper wastewater from copper/nickel plating.

(Ganczarczyk, 1984)

inherent variability of mine-milling wastewaters in different locations could potentially be reduced prior to biological treatment, permitting more widespread application of the Homestake cyanide removal process.

12.2 Chemical Post-Treatment

Two techniques are described below which will find their greatest use as final or polisning steps of a multiple stage process for removing small amounts of stable to moderately stable complexed cyanides.

The first method is the most effective and involves precipitation for the removal of stable cyanide complexes. This technique is used by a number of photographic processing laboratories, where, the major cyanide bearing species is ferrocyanide (Dagon, 1978). Ferrous sulfate (or zinc sulfate) and a flocculating agent are added to precipitate the complex. The solid is removed from the photographic wastewater by centrifuging, filtering, or by settling and decanting. The precipitate is then buried in a sealed container at a chemical disposal site.

A modified precipitation technique has been reported by Mudder and Whitlock (1984a) which can be used to remove residual cationic copper concentrations to environmentally acceptable values (i.e. below 0.009 ppm). The method comprises of first adding a solution of a compound containing ferric ion (eg. ferric chloride or ferrous sulfate) in an amount equal to at least five times the stoichiometric amount required to form the ferric salts of the cuprocyanide and cupricyanide anions, while maintaining the pH of the

wastewater below five to prevent the formation of ferric hydroxide. To encourage precipitation of the ferric cupro- and cupri-cyanide compounds, present at low concentrations, a second soluble compound is added. The sodium, potassium or calcium salts of the hydroxides, bicarbonates, carbonates, or sulfides may be used. Precipitation is achieved by adjusting the pH to approximately seven or above, causing the formation of ferric hydroxide. The remaining free cupric cation forms cupric hydroxide which is also precipitated. Flocculents can be added to accelerate the formation of the aggregates. Ferric chloride/polymer is already added to the final effluent stream at Homestake Gold Mines to flocculate the biomass. With suitable design modifications it would be possible, if necessary, to achieve the removal of residual levels of copper and iron cyanides.

A second method which may be utilized for the removal of complexed cyanides involves the use of activated carbon. The affinity of activated carbon for complexed cyanides has been documented (Ingles, 1981). However, this method has not been reported in the treatment of gold mill wastewaters. Further investigations would be necessary to test the effectiveness of this adsorbent in the final polishing step of an overall treatment scheme.

13.0 PROCESS DESIGN AND COSTING OF CYANIDE REMOVAL FROM A GOLD MINE POND EFFLUENT USING AN RBC

An RBC treatment plant was designed and costed for the pond effluent from mine QA (see Table A-7 of Appendix A). The flowrate of the pond effluent was 300,000 igpd (1,363 m^3/d). The concentrations of total cyanide and thiocyanate were 13 mg/L and 64 mg/L, respectively. The treated water must meet the effluent guidelines listed in Table 5-2A.

13.1 Process Design

A schematic diagram of the treatment process is shown in Figure 13.1. Briefly, the process includes a chemical dosing system for $NaHCO_3$ and/or H_3PO_4 and a set of RBC modules followed by a clarification train. The clarification system includes a polymer addition system, rapid mix and flocculation chambers, a clarifier, and multimedia filters.

The RBC design was based on Homestake's pilot plant work with a 0.5 m diameter disk. Homestake obtained a total cyanide destruction rate of 8.52 mg CN/d/ft^2. To obtain the same cyanide destruction rate for mine QA's pond effluent, 1,800,000 ft^2 of RBC support media will be required.

The design for the balance of the equipment followed standard wastewater treatment design methods.

The subcomponent design specifications are listed in Table 13.1.

13.2 Costing

The construction, operating and maintenance costs for the RBC were obtained from Envirex Inc. (Millwauke, Wisconsin). The costs in U.S. dollars were converted to Canadian dollars.

The construction, operation and maintenance costs for the balance of the equipment were obtained from U.S. EPA cost tables (EPA-600/2-79-162C). The costs from EPA, in 1978 U.S. dollars, were updated to 1985 by ENR indices and converted to Canadian dollars.

The cost of the treatment plant is summarized in Table 13.2. Due to the lack of hard data for design and costing, the costs listed in Table 13.2 can only be considered as budget costs.

Table 13.3 lists the items that were included in and items that were excluded from the costing. The detailed capital costs are listed in Table 13.4 and the detailed operation and maintenance costs in Table 13.5.

TABLE 13.1

FUNCTIONAL PROCESS SPECIFICATIONS FOR CYANIDE DESTRUCTION

Pondwater Flowrate:	1,362 m^3/d

Chemical Addition

Solution Preparation Tank:	550 L
Dosing Mixer:	in line

RBC

Total Media Area:	1,800,000 ft^2
9 Standard Density Media Units:	100,000 ft^2 each
6 High Density Media Units:	150,000 ft^2 each

Package Clarification System

Flocculation Chamber:		
	volume:	1 m^3
	retention time:	20 minutes
	G:	20 sec^{-1}
Clarifier:		tube settler
Overflow Rate:		6.1 m/d
Filter:		mixed media
	filter area:	11.6 m^2
	surface loading:	4.88 m/h
	media depth:	1 m
Filter Backwash:		
	surface loading:	50 m/h
	backwash duration:	10 minutes
	flow rate:	10 m^3/minute
	reservoir volume:	100 m^3

TABLE 13.2

COST SUMMARY

Item		Construction Cost $	O & M Cost $/year
Chemical addition		12,500	2,000
RBC		1,841,700	48,900
Clarification system		433,500	101,910
		---------	-------
	TOTAL	2,287,700	152,810

TABLE 13.3

LIST OF ITEMS FOR COSTING BASIS

i) **Subsystem: Chemical Addition**

- items included in construction costs:
  mixers, tanks metering pumps, housing
- items included in O & M costs:
  electric power, building energy, replacement parts, labour
- items excluded from costing:
  $NaHCO_3$, H_3PO_4

ii) **Subsystem: RBC**

- items included in construction costs:
  15 RBC modules, fibre glass covers, installation, transportation
- items included in O & M costs:
  replacement parts, electrical power, labour
- items excluded from costs:
  piping to and from RBCs, heating of pond water

iii) **Subsystem: Clarification System**

- items included in construction costs:
  polymer addition system, rapid mix chamber, flocculation chamber, clarifier, mixed media filter, pumps, mixers, mixing tanks, disinfection system, instrumentation, controls, housing
- items included in O & M costs:
  electrical energy, replacement parts, labour
- items not included in costing:
  piping from RBCs, discharge piping, chemicals

TABLE 13.4

CAPITAL COSTS FOR THE RBC CYANIDE DESTRUCTION PROCESS

EQUIPMENT	UNIT COST $	COST $
Chemical Addition System		12,500
RBC		1,841,700
Standard density media modules (9)	56,000	504,000
High density media modules (6)	67,200	403,200
Fiberglass covers (15)	7,000	105,000
Installation (15)	49,000	735,000
Transportation (15)	6,300	94,500
Package Clarification System		433,500
Escavation and site work		656
Manufactured equipment		172,029
Concrete		3,996
Labor		34,093
Pipe and valves		8,417
Electrical and instrumentation		58,186
Housing		98,611
Miscellaneous and contingency		57,512
System Total		2,287,700

TABLE 13.5

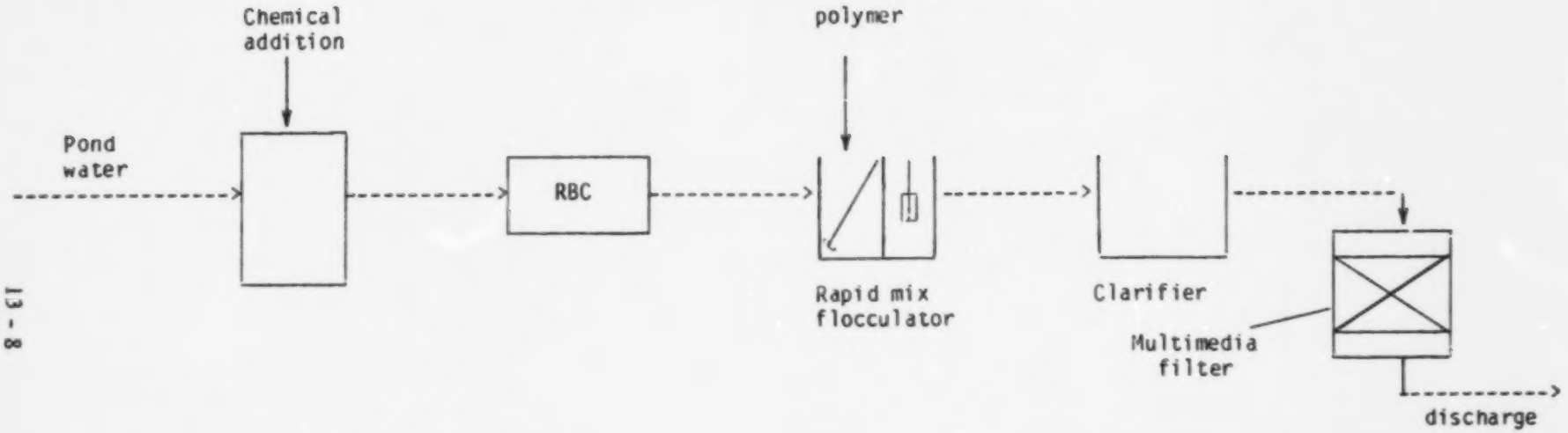
OPERATION AND MAINTENANCE COSTS FOR

THE RBC CYANIDE DESTRUCTION PROCESS

Equipment	Amount Required	Unit Cost	Cost $/year
Chemical Addition System			2,000
RBC			48,900
Maintenance	15x32 h/yr	$25/h	12,000
Replacement parts	15	$1,316/yr	19,740
Power	15x3.5 Hp	$.05/kw-h	17,160
Package Clarification System			101,910
Process energy	11,000 kw-h/yr	$.05 kw-h	550
Building energy	210,000 kw-h/yr	$.05 kw-h	10,500
Maintenance materials			3,360
Labor	3500 hr/yr	$25/hr	87,500
System Total			152,810

FIGURE 13.1

SCHEMATIC DIAGRAM OF TREATMENT PLANT



14.0 LEGAL ASPECTS

Two patents relating to the biological destruction of cyanide using the rotating biological contactor were filed by Mudder and Whitlock, on behalf of the Homestake Mining Company, April 3, 1984 (U.S.#4,440,644) and July 24, 1984 (U.S.#4,461,834). A third patent has been filed but was not available for review during the preparation of this report. The first patent claims:

i) A process for the biological degradation of cyanides, thiocyanates and metal cyanide complexes in an aqueous waste wherin organic matter dissolved in said waste acts as nutrients for growth of an aerobic flora, said process comprising:

acclimating in said aerobic flora at least one microoganism of the strain Pseudomonas paucimobilis mudlock, ATCC accession no. 39204; and contacting the aqueous waste with the aerobic flora to degrade the cyanides, thiocyanates, and metal cyanide complexes to environmentally acceptable products.

ii) A process as in claim 1, wherein the aqueous waste is contacted with the aerobic flora in a rotating biological contactor where the flora is attached to rotating discs which carry the flora into the aqueous waste during a portion of their rotation and expose the flora to air during the remaining portion of rotation.

iii) A process as in claim 1, wherein the aqueous waste is contacted with the aerobic flora in an activated sludge system where the flora and waste are alternatively agitated

and allowed to settle with continuous aeration.

The second patent claims only:

iv) A biologically pure culture of Pseudomonas paucimobilis mudlock, ATCC accession No. 39204.

The only claims made therefore cover the use of the particular subspecies of microorganism mutated and isolated from the species Pseudomonas paucimobilis by Homestake. A licensing agreement would be necessary if one desired to use the Homestake strain of microorganism, presumably available only from ATCC or Homestake. A respresentative of Homestake has expressed an interest in negotiating a licensing agreement once the suitability of the microorganism and process have been demonstrated. There should be no need for licensing agreements if one were to take a standard strain of Pseudomonas paucimobilus and mutate and select a microorganism appropriate for cyanide destruction from the general species.

Rotating Biological Contactor technology is generally available and, aside from the use of specific designs of systems which may have general patents for wastewater treatment applications, there should be no legal limits to the application of this technology.

15.0 SUMMARY AND CONCLUSIONS

An assessment of the literature, pertaining to the biological treatment of cyanide bearing wastewaters from mineral processing effluents, was completed. Biological treatment processes, reported to remove cyanide included: trickling filters, activated sludge, extended aeration, fluidized beds, and rotating biological contactors. The majority of work has been done on aerobic systems. Particular attention was given to extracting the following information:

i) The chemical characteristics of the wastewater streams to be treated (cyanide levels, form of cyanide, heavy metal concentrations, variability, concentrations of other chemical species).

ii) The characteristics of the microorganisms (rate of growth, nutrient requirements, cyanide concentrations tolerable, rate of cyanide uptake, type of cyanide degradable, optimum pH and temperature ranges for growth, inhibitors).

iii) The process characteristics (loading rates permitted, sensitivity to shock loads, fate of cyanide in the system, sludge setteability, availability of nutrients and oxygen, biomass control).

15.1 Summary of Process Related Conclusions

i) The observations of most investigators indicate that the thermodynamic stability of the metal complex cyanide is an important factor determining biodegradability. Very stable metal cyanide complexes, such as those of iron and cobalt, were not

readily biodegradable in most studies. However, strongly bound metal cyanide are less toxic than weakly bound complexes and have been reported to pass through biological treatment systems without inhibitory effects. Moderately stable complexed cyanides were reported to be partially biodegradable and free cyanides were completely biodegradable. Recent evidence, gathered by Mudder and Whitlock (1984d), suggests that metal cyanide complexes may be removed through biological oxidation and adsorption onto the biomass.

ii) In aerobic biological treatment systems (activated sludge, extended aeration) stripping is the major removal mechanism which accounts for 60-80% of the cyanide removed. Biological metabolism ranks second in importance, and is responsible for 20-40% of the cyanide removed. Adsorption and chemical reaction with substrates remove less than 15% of the cyanide. Some investigators have observed that metabolism predominates below cyanide concentrations of 40-60 mg/L. The predominant removal mechanism in other biological systems has not been established.

iii) In general, bacteria which metabolize free and weakly complexed metal cyanides are indigenous to cyanide bearing soils. Most are aerobic and heterotrophic, although a few autotrophs have been identified. The need for an external carbon source, in the form of glucose or sewage, is therefore dependent upon the organism used. Cyanide nitrogen is used as a partial source of nitrogen for both heterotrophic and autotrophic organisms.

iv) Several investigators (Mudder and Whitlock, 1983; Gaudy et. al., 1982; Pettet and Mills, 1954) reported that cyanide

assimilating organisms are slow growing but rapidly degrade cyanide. Systems capable of biological decomposition of cyanide may be quite sensitive to fluctuation of the input concentration and load. Long acclimitization periods were usually required to establish a suitable biomass. However, system recovery was usually rapid following shock loadings of cyanide (step changes of 5 mg/L or greater). Since cyanide degrading microorganisms are, in general, slow growing, possible washout or takeover are considerations in the selection of a suitable biological reactor. To maintain an adequate inventory, a fixed film process is recommended.

v) Microorganisms in a mixed population, such as those found in a sewage treatment plant, may be adapted to the degradation of any waste. Another alternative is to inoculate a mixed microbial population with one of the many organisms reported to degrade cyanide (see Table 7.1.1), or, a pure culture itself can be used.

vi) Metals toxicity did not appear to be a problem at low concentrations in short term studies. However, long term accumulation of heavy metals has been reported to be fatal to the biomass in an activated sludge system studied by Homestake. Methods of dealing with long term accumulation of heavy metals should be given serious consideration in the selected design.

vii) The rotating biological contactor appears to be a good candidate process for biodegradation studies. A licensing agreement would be required should the Homestake isolate, Pseudomonas paucimobilis mudlock, be used in the process.

15.2 Summary of Sources and Treatability of Cyanide Bearing Mineral Processing Effluents

viii) Cyanide bearing effluents are produced by five mineral processing industries:

- Gold milling barren bleeds, tailings repulp and tailings impoundment streams.
- Silver milling barren bleeds, tailings repulp and tailings impoundment streams.
- Base metal sulfide flotation tailings
- Coke oven and blast furnace blowdown wastewater by-products during iron manufacturing
- Potlining leach liquors from the electrolytic cells used in the production of aluminum from bauxite.

ix) Characteristics of gold mill wastewaters vary widely and few generalizations can be made. Consequently, the optimum operating variables of a selected process would need to be determined for a specific site. The gold mill barren bleed stream (40-700 ppm cyanide) must be diluted or treated chemically before biological treatment. The tailings repulp slurry (13-280 ppm cyanide) may be amenable to biological degradation with minimal pretreatment (eg. filtration). For optimum biological treatability, the SCN^-/CN^- ratio should be large and the fraction of free cyanides should be as close as possible to unity. Polysulfide conversion has great promise as a means of partial pretreatment to control the SCN^-/CN^- ratio and can simultaneously reduce the concentration of complexed cyanides. Thereby, the inherent variability of gold milling wastewaters may be reduced, permitting more widespread

application of a selected biological process under conditions less favourable than at Homestake.

x) Effluents from froth flotation of base metal cyanides contain tightly bound thermodynamically stable cyanides (0-40 ppm), such as metal hexacyanoferrates, which cannot be effectively degraded by biological means.

xi) The biological treatment of cyanide bearing iron and steel industry wastewaters using activated sludge, fluidized beds and rotating biological contactors is well established.

xii) Potlining leach liquors from the aluminum industry are too dilute (approximately 1 ppm cyanide) and too variable to treat biologically.

16.0 RESEARCH AND PROCESS DESIGN NEEDS

Further research should be directed in the following areas:

i) A survey should be conducted to locate sources of warm water process streams within the mine and their respective volumes. The feasibility of using these streams for heating value or as dilution streams should be evaluated. Examples include steam condensate, minewaters, cooling tower waters, barren bleed, etc. The cost of supplemental heating, if required, should also be assessed.

ii) Locally collected microfauna at various gold milling sites should be tested for cyanide removal ability. It may be possible to isolate an organism capable of thriving at colder temperatures. The types of organisms, most suitable for attached growth, should also be established; the development of a microbial "soup" of cyanide degrading organisms should also be carried out and the nutrient requirements established.

iii) Methods to recover cyanide from the barren bleed should be investigated.

The following studies are recommended in order to obtain process design information and operating data prior to application of the selected bioreactor.

iv) Mass balances should be performed in order to determine the cyanide fractions stripped, metabolized, adsorbed on the biomass, and removed by chemical reaction.

v) The cyanide and thiocyanate concentrations should be varied in order to determine the range of acceptable SCN^-/CN^- ratios for optimum biotreatment (the wastewater stream can be spiked with a particular component, as necessary, to permit this). Lime-sulfur pretreatment should be investigated as a means of controlling this ratio.

vi) The RBC performance should be evaluated with respect to hydraulic and cyanide loading in order to determine the shape of the operating curves. A range of optimum hydraulic and cyanide loadings should be established. The effect of shock loadings, temperature and pH should be investigated.

vii) The need for a supplementary carbon source (eg. sewage, soda ash) should be assessed. If needed, availability to the mine, will be an important consideration in determining the form in which it should be supplied.

viii) The resulting biomass should be examined in order to determine the fate of metallic species and possible economic benefits of recovering metallic species. For example, Homestake has reported the recovery of gold from the spent biomass.

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APPENDIX A

CHEMICAL CHARACTERISTICS OF CANADIAN GOLD MILL EFFLUENTS

TABLE B1

PROVINCE OF ONTARIO

[illegible]

MINE	pH	CONC. (mg/l)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	SULPHATES SO4	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
04	[illegible]	[illegible]	822	[illegible]	[illegible]	[illegible]	[illegible]	0.0	N/A	182	8.9	98.1	51	[illegible]	140.1	140.0	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
05	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
06	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
07	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	N/A	[illegible]	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
08	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	N/A	[illegible]	0.5	0.1	22	[illegible]	0.0	[illegible]	[illegible]	0.44	0.460	0.01	[illegible]	[illegible]

TABLE B2

PROVINCE OF ONTARIO

REFUSE FEED STREAM

MINE	pH	CONC. (mg/l)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	SULPHATES SO4	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
03	[illegible]	[illegible]	N/A	N/A	N/A	[illegible]	5000	[illegible]	N/A	2000	9.2	100	[illegible]	[illegible]	120.0	82.0	2500	[illegible]	0.960	[illegible]	1.50	0.10
04	[illegible]	N/A	N/A	N/A	N/A	[illegible]	9500	280.00	N/A	920	22.0	75	[illegible]	[illegible]	3.6	140.0	[illegible]	0.82	0.010	[illegible]	[illegible]	[illegible]
05	[illegible]	N/A	N/A	N/A	N/A	60	6000	19.00	N/A	475	5.5	11	[illegible]	[illegible]	3.5	[illegible]	2500	0.42	0.090	[illegible]	[illegible]	[illegible]
06	[illegible]	N/A	N/A	N/A	N/A	[illegible]	[illegible]	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
07	[illegible]	[illegible]	N/A	N/A	N/A	[illegible]	[illegible]	[illegible]	N/A	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

07 NOT SAMPLED

08 NOT SAMPLED

ALL UNITS: PPM EXCEPT AS NOTED

SOURCE: [illegible] TABLE FOR ONTARIO DATA.

Reference: MOE, private communication

TABLE A3

PROVINCE OF ONTARIO

MINE WATER STREAM

MINE	pH	COND. (µmhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
3A	7.5	N/A	750	4	71.	177	1900	<0.01	N/A	220	4.1	5.70	48.00	<0.01	2.8	420	0.28	0.11	0.025	0.0e	<0.06	0.02
3B	7.7	1e00	1710	20	169	240	570	0.20	N/A	540	<0.1	9.80	0.05	<0.01	0.1	0.25	2.8	<0.04	0.25	0.49	<0.06	0.04
3C	7.8	2010	2450	10	2472	191	900	<0.01	N/A	1100	N/A	2.20	0.30	<0.01	0.14	0.07	1.1	<0.04	0.019	0.42	<0.0e	<0.02
3D	7.9	N/A	660	<10	660	102	163	<0.01	N/A	240	0.5	1.00	<0.01	<0.005	0.36	0.04	0.20	<0.02	0.056	0.02	<0.03	<0.02
3E	NOT SAMPLED																					
3F	7.9	N/A	N/A	2	N/A	N/A	N/A	<2.00	N/A	2.2	0.02	0.20	0.02	<0.01	0.0	0.02	0.12	<0.01	0.01e	<0.01	<0.0	0.08
3G	7.1	N/A	N/A	1	N/A	N/A	N/A	0.01	N/A	4.0	0.02	0.20	0.01	<0.01	<0.1	<0.01	0.11	0.01	0.012	<0.01	<0.1	0.09

TABLE A4

PROVINCE OF ONTARIO

FINAL EFFLUENT STREAM

MINE	pH	COND. (µmhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
3A	7.5	N/A	e30	<15	585	190	190	<0.01	N/A	210	1.2	2.2	0.02	<0.005	0.02	<0.01	0.44	<0.02	0.022	0.03	<0.03	<0.02
3B	7.8	2725	2560	15	2545	83	1300	12.50	N/A	1365	<0.1	17.0	0.21	<0.01	0.28	17.00	0.44	<0.04	0.006	0.11	<0.06	0.07
3C	7.9	N/A	790	15	775	57	300	3.50	N/A	340	4.0	e.8	0.17	<0.005	0.81	2.60	0.80	0.05	0.016	0.16	<0.03	0.11
3D	8.2	N/A	255	<15	>240	79	98	2.46	N/A	70	4.6	7.9	0.20	<0.01	0.98	0.90	0.72	0.05	0.3e0	<0.04	<0.06	0.65
3E	8.3	1325	910	15	895	259	442	N/A	N/A	200	N/A	5.0	0.08	<0.01	0.06	1.30	0.52	0.04	0.003	1.80	<0.06	0.09
3F	9.2	N/A	N/A	1	N/A	N/A	N/A	<0.01	N/A	375	1.5	8.1	20.00	<0.01	N/A	12.00	2.20	0.58	4.900	<0.01	<0.1	N/A
3G	7.6	N/A	N/A	10	N/A	N/A	N/A	0.20	N/A	68.5	0.5	1.5	0.19	<0.01	N/A	0.44	0.99	0.04	N/A	0.17	<0.1	N/A

Reference:MOE, private communication

TABLE A5

[illegible]

[illegible]

MINE	pH	COND. mS/cm	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	THIOCYANATES (SCN)	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) ppb
DA	11.8	N/A	N/A	N/A	N/A	N/A	N/A	210	70	410	N/A	4.7	N/A	64.1	N/A	1.7	11	0.37	0.222	N/A	N/A	<0.1	N/A
DB	12.0	N/A	N/A	N/A	N/A	N/A	N/A	200	22	190	N/A	19	N/A	17.9	N/A	2.9	73	25.7	0.322	<0.03	N/A	<0.1	N/A
DC	11.7	N/A	N/A	N/A	N/A	N/A	N/A	240	145	58	N/A	28	N/A	62.5	N/A	10	6.7	21.4	0.222	<0.3	N/A	<0.1	N/A
DD	11.8	N/A	N/A	N/A	N/A	N/A	N/A	84	84	42	N/A	18	N/A	13.9	N/A	0.28	0.1	0.36	<0.01	<0.07	N/A	<0.1	N/A
DE	11.9	N/A	N/A	N/A	N/A	N/A	N/A	103	101	210	N/A	9.2	N/A	10.2	N/A	1.54	26.2	0.07	0.161	0.19	N/A	<0.1	N/A

TABLE A6

[illegible]

[illegible]

MINE	pH	COND. mS/cm	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	THIOCYANATES (SCN)	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) ppb
EA	11.6	N/A	N/A	N/A	N/A	N/A	N/A	160	150	120	N/A	N/A	N/A	22.9	N/A	0.52	1.0	0.290	0.13	N/A	N/A	0.1	N/A
EB	11.1	N/A	N/A	N/A	N/A	N/A	N/A	22	22	24	N/A	N/A	N/A	6.1	N/A	0.50	12.2	5.400	0.07	<0.02	N/A	<0.1	N/A
EC	11.2	N/A	N/A	N/A	N/A	N/A	N/A	67	60	19	N/A	N/A	N/A	16.3	N/A	2.40	4.9	7.100	0.19	<0.02	N/A	<0.1	N/A
ED	11.0	N/A	N/A	N/A	N/A	N/A	N/A	41	21	16	N/A	N/A	N/A	1.0	N/A	0.10	0.4	0.090	0.02	<0.03	N/A	<0.1	N/A
EE	11.7	N/A	N/A	N/A	N/A	N/A	N/A	85	79	74	N/A	N/A	N/A	1.2	N/A	0.65	15.0	0.117	0.08	<0.03	N/A	<0.1	N/A

Reference:EPS, Montreal, private communication

TABLE A7

PROVINCE OF QUEBEC

MINE WATER DATA

MINE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	THIOCYANATES CNS	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
AA	8.7	N/A	1.3	N/A	N/A	N/A	N/A	0.19	<0.5	<2.0	N/A	11.0	N/A	0.11	N/A	0.18	0.160	26.80	0.02	<0.03	N/A	<0.1	N/A
AB	8.1	N/A	N/A	N/A	N/A	N/A	N/A	0.06	<0.5	<2.0	N/A	5.1	N/A	0.02	N/A	0.06	0.070	2.80	0.08	<0.03	N/A	<0.1	N/A
AC	8.0	N/A	N/A	N/A	N/A	N/A	N/A	0.07	<0.5	<2.0	N/A	0.3	N/A	0.02	N/A	0.12	0.020	1.90	0.03	<0.03	N/A	<0.1	N/A
AD	7.7	N/A	N/A	N/A	N/A	N/A	N/A	0.12	<0.5	<2.0	N/A	0.6	N/A	0.07	N/A	0.06	0.079	4.10	0.23	<0.03	N/A	<0.1	N/A
AE	7.9	N/A	N/A	N/A	N/A	N/A	N/A	0.02	<0.5	<2.0	N/A	0.7	N/A	0.11	N/A	0.03	0.080	0.43	0.02	<0.03	N/A	<0.1	N/A

TABLE A8

PROVINCE OF QUEBEC

FINAL EFFLUENT STREAM

MINE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	FREE CYANIDE	THIOCYANATES CNS	SULPHATES (SO4)	FREE AMMONIA	TOTAL KJELDAHL	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANESE (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
BA	7.6	N/A	N/A	17	N/A	N/A	N/A	12.00	0.6	64.0	N/A	7.1	N/A	0.81	N/A	0.38	2.350	0.71	0.050	<0.03	N/A	<0.01	N/A
BB	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.20	<0.5	5.0	N/A	0.4	N/A	0.43	N/A	0.10	0.330	0.36	0.016	<0.03	N/A	<0.1	N/A
BC	8.2	N/A	N/A	N/A	N/A	N/A	N/A	0.20	0.2	0.5	N/A	1.8	N/A	0.66	N/A	0.08	1.060	1.43	0.073	<0.03	N/A	<0.1	N/A
BD	8.2	N/A	N/A	N/A	N/A	N/A	N/A	3.40	0.8	8.0	N/A	N/A	N/A	0.18	N/A	0.07	2.260	5.18	<0.033	<0.03	N/A	<0.1	N/A
BE	7.2	N/A	N/A	N/A	N/A	N/A	N/A	0.20	<0.5	<2.0	N/A	13.0	N/A	0.09	N/A	0.03	0.020	3.57	0.141	<0.03	N/A	<0.1	N/A

Reference:EPS, Montreal, private communication

TABLE A9

PROVINCE OF BRITISH COLUMBIA

BARRIER BLEED STREAM EFFLUENT

DATE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	CYANIDE (WAD)	THIOCYANATES CNS	CYANATE (CNO)	SULPHATES (SO4)	FREE AMMONIA	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANES (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
MAY 3/83	11.2	N/A	296	<5	N/A	N/A	415	476	468	1100	11	556	17	10e	<0.02	1.5	111	46.9	1.12	<0.5	0.01	<0.2	<0.5
JULY 11/83	11.1	2540	1970	<5	N/A	N/A	377	224	221	61.3	13.4	338	N/A	44.9	<0.002	0.16	21.6	2	0.219	0.07	<0.001	<0.02	N/A
JULY 26/83 (a.m.)	11.1	N/A	5730	<5	N/A	N/A	487	508	331	1960	N/A	359	10.7	24.2	<0.01	0.9	111	105	0.89	<3	0.039	<0.1	<0.0002
JULY 28/83 (p.m.)	11.3	N/A	4750	7	N/A	N/A	353	446	354	1586	N/A	504	9.89	2a.9	<0.1	64	109	455	1.2	<3	7.95	<1	<0.0002

TABLE A10

PROVINCE OF BRITISH COLUMBIA

REPULPED TAILINGS STREAM

DATE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	CYANIDE (WAD)	THIOCYANATES CNS	CYANATE (CNO)	SULPHATES (SO4)	FREE AMMONIA	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANES (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
MAY 3/83	11.1	N/A	14100	294	N/A	N/A	2440	198	55.8	580	29.1	420	9.5	742	14.3	6	198	12900	618	3e7	410	2e8	7
JULY 11/83	10.8	640	71000	24000	N/A	N/A	117	30	21	18.2	1.98	1960	N/A	211	5	<20	18e	17800	59	8e	771	15.	N/A
JULY 26/83 (a.m.)	9.9	N/A	216000	210000	N/A	N/A	44e00	409	244	1528	N/A	79e	6.94	295	3.7	12	174	11000	19	12.	1e2	95	N/A
JULY 28/83 (p.m.)	10.9	N/A	217000	52000	N/A	N/A	150	160	52	584	N/A	169	2.69	484	10.2	26	369	55e00	67	470	779	158.	N/A

Reference:EPS, Vancouver, private communication

TABLE A11

PROVINCE OF BRITISH COLUMBIA

FINAL EFFLUENT STREAM

DATE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY CaCO3	TOTAL HARDNESS	TOTAL CYANIDE	CYANIDE WAD	THIOCYANATES CNS	CYANATE (CNO)	SULPHATES (SO4)	FREE AMMONIA	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANES (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
MAY 3/82	11.9	N/A	19900	317	N/A	N/A	3680	86.9	55.8	989	29.1	430	9.5	740	14.3	6	198	12000	≤18	367	410	268	<3
JULY 11 82	8.2	4790	154000	220000	N/A	44	417	0	0.28	25.3	177	2265	7.85	221	3	<4	38	11900	40	69	287	120	N/A
JULY 12/82 (p.m.)	9.3	N/A	318000	260000	N/A	N/A	66900	234	50	1109	N/A	1330	4.25	457	4.6	<6	194	16400	19	150	245	140	N/A

* SAMPLE PRODUCED NON-CYANIDE-LIKE TRACE UPON UV SCANNING.

TABLE A12

PROVINCE OF BRITISH COLUMBIA

MINE WATER STREAM

DATE	pH	COND. (mhos)	TOTAL SOLIDS	SUSPENDED SOLIDS	DISSOLVED SOLIDS	ALKALINITY (CaCO3)	TOTAL HARDNESS	TOTAL CYANIDE	CYANIDE (WAD)	THIOCYANATES CNS	CYANATE (CNO)	SULPHATES (SO4)	FREE AMMONIA	ZINC (Zn)	CADMIUM (Cd)	NICKEL (Ni)	COPPER (Cu)	IRON (Fe)	COBALT (Co)	ARSENIC (As)	MANGANES (Mn)	LEAD (Pb)	MERCURY (Hg) (ppb)
MAY 3/82	7.8	N/A	717	314	N/A	N/A	193	<0.03	<0.03	<2.0	9.99	122	14	1.09	0.015	<0.02	0.355	43.7	0.364	0.14	1.01	0.44	<0.05

CYANIDE

WAD = WEAK ACID DISSOCIABLE (refers to all cyanide forms except those of Fe, Co, Au)

TOTAL = All forms of cyanide except Co and Au.

Reference: EPS, Vancouver, private communication

TABLE A13

NORTH WEST TERRITORIES

WASTE STREAM	pH	TSS	TOTAL CYANIDE	ZINC (ZN)	COPPER (CU)	IRON (FE)	ARSENIC (AS)
CONVENTIONAL BARREN BLEED	11.3	<2	360	102	108	12.6	14
CARBON PLANT BARREN	8.5	220000	520	840	665	52500	10000
MINE WATER	7.8	33	0.25	N/A	N/A	N/A	7.2
FINAL EFFLUENT	8.6	3.3	15.3	N/A	N/A	N/A	19.7

TABLE A14

WASTE STREAM	FLOW	CNT	SCN	CNF/CNT	SCN/CNT
CONVENTIONAL BARREN BLEED	71000	360			
CARBON PLANT BARREN	4000	520			
MINE WATER	420000	0.25			
FINAL EFFLUENT	915000*	15.3			

* DECANTED FOR SIX MONTHS ONLY.

Reference: Wiskel, B.W.; Price, L.S., and Erkku, H.; "Treatment of Giant Yellowknife Mines Effluent for Reduction of Cyanide and Arsenic Pilot Plant Operation at Giant Yellowknife Mines Ltd." (1976-1977).

APPENDIX B

SUMMARY OF PROCESS PARAMETERS USED IN VARIOUS TREATABILITY STUDIES OF CYANIDE BEARING WASTEWATERS

TABLE B-1

ACTIVATED SLUDGE

REFERENCE: Murphy & Nesbitt (1964)

HRT: 2.2 hrs.

SRT: 11 days

SUBSTRATE LOADINGS: max: 5.95 mg CN^-/gMLVS/hr.

limit: 5 mg CN/g MLVS/hr.

AERATION RATE: 0.283 cu.m/hr air

MIXING: completely mixed

BIOMASS: 200 mg/L acclimated (seed obtained from a sewage treatment plant)

TEMPERATURE: 20°C

pH: approximately 7

PROCESS EFFICIENCY: complete CN removal

NUTRIENTS: 1000 mg/L KH_2PO_4, standard BOD dilution water

FEED: 100 mg/L CN in synthetic sewage (made of fish food)

COMMENT: Conventional activated sludge operation with sludge waste seems to keep the cells 'young'. 'Young' cells seem to be able to cope with fluctuating feed CN concentration without failure. Shock loads up to twice of existing CN loadings are permitted.

TABLE B-2

ACTIVATED SLUDGE

REFERENCE: Harden, Jones & Gauthier (1983)

HRT: 42 hrs.

SRT: 50 days

SUBSTRATE LOADINGS:

AERATION RATE: not indicated

MIXING: completely mixed

BIOMASS: 1000-2000 mg/L MLVS (acclimated mixed liquor from wastewater plant processing coke-plant effluent used as seed)

TEMPERATURE: 35°C

pH: 7.2

PROCESS EFFICIENCY: feed: coke plant wastewater spiked with 40-200 mg/L cyanide

effluent: < 0.2 mg/L

NUTRIENTS: KCl, $MgSO_4$, H_3PO_4

COMMENT: In the treatment of coke plant wastewaters, the primary difficulty is the general toxicity that occurs at higher organic loadings that decreases the efficiency of all microorganisms in the system. Phenol and thiocyanate removal were unaffected by additions of cyanide to the reactor.

TABLE B-3

EXTENDED AERATION WITH INTERNAL CLARIFIER

REFERENCE: Murphy & Nesbitt (1964)

HRT: 22.5 hrs.

SRT: 26-40 days

SUBSTRATE LOADING: upper limit: 5 mg CN/g MLVS/hr.

AERATION RATE: 0.283 cu.m/hr. air

MIXING: completely mixed

BIOMASS: varied, 3000-5200 mg/L aclimated (seed obtained from a sewage treatment plant)

TEMPERATURE: 20°C

pH: approximately 7

PROCESS EFFICIENCY: complete CN^- removal

NUTRIENTS: 1000 ml/L KH_2PO_4
standard BOD dilution water

FEED: maximum 540 mg/L CN^- in synthetic sewage (made of fish food)

COMMENT: Extended aeration method susceptible to upsets due to fluctuations in loadings as 'old cells' do not grow fast enough to cope with the sharply increased loadings.

Buildup of solids to high levels inhibits CN^- degradation.

TABLE B-4

FLUIDIZED BED - NITRIFICATION REACTOR

REFERENCE: Nutt, Melcer, Marvan and Sutton (1982)

HRT: 15.3 hrs.

SRT: 62.4 days

SUBSTRATE LOADINGS: not indicated

AERATION RATE: not indicated

MIXING: completely mixed

BIOMASS: 14.5 g/L

TEMPERATURE: 25.5 - 28 deg.C.

pH: 7.0 - 7.4

PROCESS EFFICIENCY: feed: 8.0 + .4 mg CN/L (coke oven wastewater)

effluent: 6.1 + 1.4 mg CN/L

NUTRIENTS: H_3PO_4, $NaHCO_3$

FEED: coke plant wastewater

COMMENT: effective reactor volume: 210 L

bio support media: quartzite sand (d_{10}) = .48 mm

uniformity coefficient (d_{60}/d_{10}) = 1.23

recycle ratio: 270

Process as operated does not meet 0.025 mg CN/L residual level. Organics removal is main effort of study, cyanide removal a side line.

SRT seems very long for effective cyanide removal. If CN removal emphasized the system could be made to work.

TABLE B-5

ROTATING BIOLOGICAL CONTRACTOR, 2m PILOT PLANT

REFERENCE: Mudder and Whitlock (1984)

SRT: not indicated

SUBSTRATE LOADINGS: 0.1 - 0.38 g/sq.m/d

AERATION RATE: 600 SCFM = 17 cu.m/min. (for "stripping" of biomass)
2.5 SCFM = 0.07 cu.m/min. (supplemental aeration to each stage of pilot plant)

DEGREE OF MIXING: not indicated

BIOMASS: nitrofying bacteria
Pseudomonas paucimobilis mudlock

TEMPERATURE: 11 - 20°C

pH: approxiamtely 6.5

PROCESS EFFICIENCY: feed: 6.5 + mg CN/L (combined tailings impoundment wastewater and mine water from a gold mill)
effluent: 0.35 + 0.1 mg/CN/L

NUTRIENT: Na_2CO_3 (soda ash)

H_3PO_4

COMMENT: Limited data presented. Na_2CO_3 added to waste probably as pH buffer rather than carbon source (also supplemental alkalinity). As operated this system would not meet 0.025 mg CN/L residual level. An organic carbon supplement required, probably domestic wastewater. System should be operated in the nitrification mode. The effluent of the RBC was clarified and passed through a sand filter.